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ABSTRACTS

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BUREAU OF CHEMICAL ABSTRACTS.

A. PURE CHEMISTRY.

PART I.

Organic Chemistry.

Substitution Reactions in Organic Chemistry. B. N. MENSCHUTKIN (*Ann. Inst. Analyse Physico-Chim.*, 1922, **2**, 61—95).—A theoretical paper in which the nature of substitution reactions is first discussed and it is pointed out that the study of binary mixtures by the thermal method often gives valuable indications regarding the mechanism of such reactions. The mechanism of Friedel and Crafts' reaction, and more especially the part played by the aluminium chloride, is then examined in detail. G. A. R. K.

Number of Atomic Rings in Molecules. H. DECKER (*Z. physikal. Chem.*, 1923, **107**, 111—118).—A theoretical paper in which the author deduces equations to give the number of rings contained in organic and other compounds of stated molecular formula. The consideration is based on Mendeléev's formula for the relationship between the number of primary, quaternary, and tertiary carbon atoms in the members of the ethylene series of hydrocarbons, namely, $pr=te+2qu$, where pr, te, and qu represent, respectively, the number of primary, tertiary, and quaternary carbon atoms. If R represents the number of rings, ethylene itself, and all double linkings being regarded as two-membered rings, then $R=1-1/2pr+1/2te+qu$. The number of rings in any hydrocarbon of the formula C_nH_m is given by $R=1-1/2m+n$. In any organic compound of the formula $C_nH_mO_oN_p^{III}N_q^{V}$, where the oxygen is all bivalent, the number of rings is given by $R=1-1/2m+1/2p+n+3/2q$. In a compound of the molecular formula $E_m^{I}E_o^{II}E_p^{III}E_n^{IV}E_q^{V}E_r^{VI}E_s^{VII}E_t^{VIII}$, where $E^{I}E^{II}$, etc., represent elements of one, two, three . . . eight valencies and m, n, . . . represent the number of atoms of such elements, the number of rings is given by the formula $R=1-1/2m+1/2p+n+3/2q+2r+5/2s+3t$. For open-chain compounds the

relationship $m=6t+5s+4r+3q+2n+p+2$ is true. The usual formula for the paraffins C_nH_{2n+2} corresponds with the formula $E_t^{VIII}E_s^{VII}E_r^{VI}E_q^{V}E_n^{IV}E_p^{III}E_o^{II}E_m^{I}$, where $m=6t+5s+4r+3q+2n+p+2$ for compounds of any elements. The formula for hydrogen derivatives of any element E^x, which is an open chain and contains y atoms of E^x, x being the valency, is $E^xH_{(x+2)y+2}$. The formula of the polycyclic hydrogen derivative is given by $E^xH_{(y-2)y+2-2R}$, where R is the number of rings. The entrance of two univalent atoms into a molecule ruptures a ring, the entrance and removal of bivalent atoms do not affect the number of rings, the entrance of two tervalent atoms brings about the formation of a ring, the entrance of one quadrivalent atom forms one ring, the entrance of two quinquevalent atoms produces three rings, the entrance of one sexavalent atom produces two rings, the entrance of two septavalent atoms produces five rings, and the entrance of one octavalent atom produces three rings. J. F. S.

The Preparation of Pure Ethylene. L. Moser and F. Lindinger (*Monatsh.*, 1923, **44**, 141—150).—The effect of adding various catalysts to mixtures in various proportions of 96% alcohol and concentrated sulphuric acid has been examined. Using molecular proportions of alcohol and acid, evolution of gas begins at 140°, but in presence of small quantities of foreign substances, evolution may begin at 125°. The purity of the gas and the proportions of ether, sulphur dioxide, and carbon dioxide were determined under various conditions, the best results being obtained by using 1 mol. of alcohol to 2 mols. of acid, adding 1·5—2·0% of copper sulphate; the yield is 15—20% at a temperature of 145—150°, the gas after careful purification containing 99·2% of ethylene.

By allowing alcohol to drop on to orthophosphoric acid (d 1·70) heated at 220°, the yield is raised to 30%, but the gas after washing contains 5% of impurities, chiefly butane. If alcohol vapour is passed over pumice saturated with pyrophosphoric acid heated at 300°, a yield of abut 90% of nearly pure ethylene is obtained. Using kaolin at a temperature of 400° in place of the pumice saturated with pyrophosphoric acid, the yield is 50—60%, and the gas contains, after washing, 2·8—3·6% of impurities.

The action of zinc on ethylene dibromide, which gives the purest gas, is conveniently carried out by warming granulated zinc with a solution of the dibromide in alcohol (15% by volume) at 40°, more dibromide being allowed to trickle in from a dropping funnel when the first evolution of gas slackens. S. I. L.

Catalytic Dehydrations and Dehydrogenations by Means of Anhydrous Zinc Sulphate. G. Brus (*Bull. Soc. chim.*, 1923, **33**, [iv], 1433—1440).—Anhydrous zinc sulphate behaves towards alcohols as a mixed catalyst, its action being both dehydrating and dehydrogenating. The latter action preponderates as in the case of zinc oxide and it is suggested that the sulphate may function as a basic salt. Its action is more marked than that of the oxide. A proportion of the aldehyde formed is condensed, but *iso*butaldehyde and *iso*valeraldehyde may be obtained readily and in good yield,

whilst glycerol yields acraldehyde by internal dehydration. The action on acetone results in the formation of a small quantity of mesityl oxide and of phorone. H. J. E.

Trichloro- and Tribromo-ethyl Alcohols. R. WILLSTÄTTER and W. DUISBERG (*Ber.*, 1923, **56**, [*B*], 2283—2286).—The phytochemical reduction of chloral and bromal is described.

A dilute solution of bromal hydrate in water containing carbon dioxide is added gradually to a solution of sucrose in water which is in the process of active fermentation by bottom yeast. Poisoning of the ferment is avoided if the total concentration of bromal hydrate and brominated alcohol is maintained below 0·2%. The products of the reaction are dibromoethyl alcohol, b. p. 70—72°/10—11 mm., d_4^0 2·33 (*dibromoethylurethane*, prisms, m. p. 90—91°), possibly monobromoethyl alcohol and tribromoethyl alcohol, prisms, m. p. 80°, b. p. 92—94°/11 mm. (*tribromoethylurethane*, prisms, m. p. 86—87°).

Trichloroethyl alcohol is produced similarly from chloral hydrate. Since the yield of alcohol is 70% of that theoretically possible, its formation must be ascribed to the addition of hydrogen, and not to disproportionation of the aldehyde. *Trichloroethyl* p-*nitrobenzoate* crystallises in domatic prisms, m. p. 71°; it is reduced by ammonium sulphide in alcoholic solution to *trichloroethyl* p-*aminobenzoate*, slender, lustrous needles, m. p. 87°, whereas hydrogen sulphide and other reagents transform it readily into ethyl *p*-aminobenzoate. *Trichloroethyl carbamate* crystallises in needles, m. p. 64—65°. H. W.

Odour and Molecular Asymmetry. J. VON BRAUN and W. KAISER (*Ber.*, 1923, **56**, [*B*], 2268—2274).—An instance is recorded in which the odour of an optically active substance differs appreciably from that of the corresponding *dl*-mixture.

dl-$\gamma\eta$-Dimethyloctanol, $CHMe_2{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, b. p. 104—105°/12 mm., d^{18} 0·838, is obtained in 80% yield by the catalytic hydrogenation of citral under medium pressure and in the presence of a nickel catalyst at about 150°. In accordance with the authors' experience of the hydrogenation of aldehydes (A., 1923, i, 1197) small amounts of a by-product, a pale yellow, viscous liquid, b. p. 189—194°/13 mm., d_4^{19} 0·892, are also produced which is regarded as the secondary *alcohol*,

$CHMe_2{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}[CH_2]_2{\cdot}CH(OH){\cdot}CH_2{\cdot}CHMe{\cdot}[CH_2]_3{\cdot}CHMe_2$.

The primary alcohol is transformed into the corresponding *acetate*, b. p. 108—109°/14 mm., d_4^{17} 0·875, from which it is regenerated with unchanged physical constants. In a similar manner, *d*-citronellal, b. p. 86—89°/12 mm., d_4^{20} 0·855, α_D about +12°, is hydrogenated to d-$\gamma\eta$-*dimethyloctanol*, b. p. 104—106°/12 mm., d_4^{19} 0·838, $[\alpha]_D$ +2° 23′, and a *substance*, b. p. about 200°/14 mm., of the approximate composition $C_{20}H_{42}O$. The possibility that racemisation occurs to a greater or less extent during the hydrogenation appears to be excluded by the observation that the properties of the product are not appreciably altered by wide variation of the experimental

conditions. The primary alcohol is transformed into its *acetate*, a liquid, b. p. 107—109°/14 mm., d_4^{17} 0·877, $[\alpha]_D$ +0° 28′, from which it is regenerated with unchanged physical properties. Its odour is more refreshing and penetrating than that of the inactive alcohol. The suspicion, however, that it is possibly contaminated with *iso*pulegol has led the authors to continue their work in the following manner.

The alcohols are oxidised to the corresponding aldehydes. dl-*γη-Dimethyloctanaldehyde* is a liquid, b. p. 79—82°/13 mm., d_4^{22} 0·823 (*semicarbazone*, needles, m. p. 92—93°), whereas the active *aldehyde* has b. p. 79—82°/13 mm., d_4^{19} 0·824, $[\alpha]_D$ +10° 2′ (*semicarbazone*, m. p. 78—79°). Both aldehydes have a very pleasant odour of lemons, but that of the inactive compound is more pleasant and intense. They are oxidised with extreme ease when exposed to air; the inactive aldehyde yields thereby an acid, b. p. 134—137°/13 mm., d_4^{18} 0·897, which closely resembles Wallach's decoic acid (A., 1912, i, 878).

dl-Dimethyloctanol is converted by fuming hydrobromic acid at 110—120° into the corresponding *bromide*, b. p. 103°/14 mm., which is transformed successively into the corresponding *nitrile*, $CHMe_2{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}CN$, a colourless liquid, b. p. 112—114°/14 mm., d_4^{18} 0·836, dl-*undecoic acid*, b. p. 149—152°/14 mm., d_4^{18} 0·897, and *ethyl* dl-*undecoate*, b. p. 120—122°/13 mm. In a similar series, *d*-dimethyloctanol is converted successively into the corresponding *bromide*, b. p. 103—105°/13 mm., d_4^{19} 1·083, $[\alpha]_D$ −5° 37′; the *nitrile*, b. p. 111—114°/14 mm., d_4^{18} 0·836, $[\alpha]_D$ +0° 30′; d-*undecoic acid*, b. p. 151—153°/14 mm., d_4^{17} 0·901, $[\alpha]_D$ −0·35°, and *ethyl* d-*undecoate*, b. p. 124—126°/14 mm., d_4^{21} 0·866, $[\alpha]_D$ +0° 12′. The possibility of racemisation during the sequence of changes is practically excluded by the observations that *d*-dimethyloctanol is regenerated unchanged from the bromide and by the hydrolysis of the nitrile and ester by acid or alkali to undecoic acid which is optically identical with the product obtained by acid hydrolysis of the nitrile. Reduction of the esters by sodium and alcohol under precisely similar conditions leads to the production of the corresponding *δθ-dimethylnonanols*, the yields being 75% and 25% in the cases of the *d*- and *dl*-compounds, respectively. The *dl*-alcohol has b. p. 110—113°/14 mm., d_4^{19} 0·834, whereas the dextrorotatory alcohol has b. p. 117—120°/15 mm., d_4^{18} 0·833, $[\alpha]_D$ +2° 7′. The physical constants of the racemic and dextrorotatory *acetates* are b. p. 124—126°/13 mm., and b. p. 124—126°/13 mm., d_4^{17} 0·866, $[\alpha]_D$ +0° 48′. The observation that the portion of the ethyl *d*-undecoate which is hydrolysed during the reduction yields an optically pure *d*-acid renders it improbable that the dimethylnonanol is partly racemised. The alcohols have a very pleasant odour resembling that of geranium leaves; the smell of the optically inactive compound is, however, more intense and less delicate than that of the active compound.

d-*γη-Dimethylnonaldehyde* is a liquid, b. p. 93—96°/13 mm., d_4^{18} 0·830, $[\alpha]_D$ +1° 12′; the corresponding *semicarbazone* has m. p. 67—69°. H. W.

The Halohydrins of Mesityl Oxide. PASTUREAU and H. BERNARD (*Bull. Soc. chim.*, 1923, [iv], **33**, 1440—1444).—Mesityl oxide readily yields halohydrins with hypochlorous, hypobromous, and hypoiodous acids. *Mesityl oxide chlorohydrin*, $OH{\cdot}CMe_2{\cdot}CHCl{\cdot}COMe$, a colourless, oily liquid, b. p. 81°/10 mm., is obtained the most easily and with the best yield. The method employed consists in the addition of mesityl oxide to a mixture of calcium hypochlorite and boric acid and extraction of the product with ether. On saponification by means of potassium carbonate, the glycol of mesityl oxide is formed. Addition of mesityl oxide to bromine water which has been kept for two days yields *mesityl oxide bromohydrin*, $CMe_2Br{\cdot}CH(OH){\cdot}COMe$, an oily, colourless, lachrymatory liquid, b. p. 73—75°/20 mm. The different constitution, as compared with the chlorohydrin, is assigned to it by reason of its lower boiling point. With potassium carbonate, it behaves similarly to the chlorohydrin. The action on mesityl oxide dissolved in ether saturated with water of iodine in presence of yellow mercuric oxide yields a mixture from which a lachrymatory liquid containing the iodohydrin may be prepared, but separation by distillation under reduced pressure is not practicable, as the substance decomposes. It has a tendency to lose hydriodic acid. Its reactions with potassium carbonate, silver nitrate, and sodium benzoate produce the glycol of mesityl oxide; with the last-named reagent the mesityl homologue of ethylene oxide is formed in addition. This substance may also be prepared by the action of silver oxide on an ethereal solution of the iodohydrin.

H. J. E.

Unsaturated Reduction Products of the Sugars and their Transformations. VII. The Anhydride of a Disaccharide from δ-Hydroxy-δ-acetylbutyl Alcohol. M. BERGMANN, A. MIEKELEY, and F. STATHER (*Ber.*, 1923, **56**, [*B*], 2255—2257).—The synthesis of a non-reducing disaccharide anhydride of the type which has been assumed to constitute the components of the complex polysaccharides is described.

Anhydro-δ-*enol*-acetylbutyl alcohol, $\begin{matrix}CH_2\text{—}O\text{—}CMe\\ |\quad\quad\quad\quad ||\\ CH_2{\cdot}CH_2{\cdot}CH\end{matrix}$, is converted by an ethereal solution of perbenzoic acid into δ-hydroxy-δ-acetylbutyl alcohol, $OH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}COMe$ (A., 1923, i, 1053). The ethereal solution is shaken with water and the aqueous extract is concentrated under diminished pressure; the residue is mixed with water, or preferably, with the condensate from the first distillation and the solvent is again evaporated, whereby the new *disaccharide anhydride*, $\begin{matrix}CH_2\text{–}O\text{—}CMe{\cdot}O{\cdot}CH{\cdot}CH_2{\cdot}CH_2\\ |\quad\quad\quad\quad

without decomposition (b. p. 268°) under atmospheric pressure. It does not reduce Fehling's or ammoniacal silver solution. It does not react with phenylhydrazine. It is hydrolysed with unusual difficulty, which may be partly due to its very sparing solubility in water. It is converted by treatment with hot 2·5*N*-sulphuric acid into a mixture of δ-hydroxy-δ-acetylbutyl alcohol anhydride, $\begin{matrix}CH_2\text{—}O\text{—}CMe\\ |\quad\quad\quad |\\ CH_2\cdot CH_2\cdot CH\text{—}\end{matrix}\!>O$, and δ-hydroxy-δ-acetylbutyl alcohol. It is transformed by methyl-alcoholic hydrogen chloride into the methyl-*cyclo*acetal of δ-methoxy-δ-acetylbutyl alcohol, $\begin{matrix}CH_2\text{—}O\text{—}CMe\cdot OMe\\ |\quad\quad\quad\quad |\\ CH_2\cdot CH_2\cdot CH\cdot OMe\end{matrix}$.

H. W.

The Behaviour of some Homologues of Acetone with Alkaline Condensing Agents. A. FRANKE and T. KÖHLER (*Annalen*, 1923, **433**, 314—326).—In the presence of cold, concentrated, aqueous alkali hydroxide solution, methyl ethyl ketone undergoes condensation to *γ-methylheptan-γ-ol-ε-one*,

$$CH_2Me\cdot CMe(OH)\cdot CH_2\cdot CO\cdot CH_2Me,$$

a colourless, mobile oil, b. p. 187—192° (slight decomp.), or 80°/about 12 mm., *oxime*, an oil, b. p. 130—138°/10 mm. If the condensation is carried out using concentrated alcoholic alkali hydroxide or sodium ethoxide solution, the product is Δ^{δ}-hepten-γ-one (cf. Becker and Thorpe, T., 1922, **121**, 1303), *oxime*, an oil, b. p. 103—104°/10 mm.; the same compound is formed if boiling aqueous alkali hydroxide is employed. The action of cold, concentrated aqueous sodium hydroxide on methyl propyl ketone gives *δ-methylnonan-δ-ol-δ-one*, a colourless, mobile oil, b. p. 99·5—100°/10 mm., whereas the product when sodium ethoxide is used is δ-methyl-Δ^{δ}-nonen-δ-one (cf. Descudé, A., 1903, i, 735), a clear, mobile oil, b. p. 198—204°, *oxime*, thick, colourless liquid, b. p. 120—122°/10 mm. Diethyl ketone does not undergo condensation in the presence of cold or boiling aqueous alkali, but in the presence of sodium ethoxide there is formed a slightly yellow *oil*, b. p. 247° (oily *oxime*, b. p. 148—149°/10 mm., from which a few crystals separate), together with a portion having b. p. 200—240°; the latter appears to be an unsaturated ketone, whilst the former only reacts slowly with bromine in chloroform solution.

Diethyl ketone condenses, but not readily, with acetaldehyde in the presence of a small quantity of dilute, aqueous alkali hydroxide, to give, apparently, *γ-methylheptan-β-ol-δ-one*,

$$CH_2Me\cdot CO\cdot CHMe\cdot CHMe\cdot OH,$$

b. p. 84—85°/10 mm.; if *iso*butaldehyde is employed, the product is *βδ-dimethylheptan-γ-ol-δ-one*, an oil, b. p. 95—96°/15 mm., which is also formed by the use of alcoholic alkali hydroxide, and from which water is eliminated by warming with anhydrous oxalic acid, to give *βδ-dimethyl-*Δ^{γ}*-hepten-δ-one*, a colourless oil, b. p. 178—183° (decomp.), or 66—69°/16 mm., *oxime*, crystals, m. p. 83°, b. p. 112°/16 mm., giving an *acetate*, a colourless oil, b. p. 125—127°/16 mm.

The hydroxy-ketones described are practically odourless, but the unsaturated ketones have powerful, characteristic odours.

W. S. N.

The Purity of αγ-Dichlorohydrin Prepared by the Action of Hydrogen Chloride on Glycerol. J. B. CONANT and O. R. QUAYLE (*J. Amer. Chem. Soc.*, 1923, **45**, 2771—2772).—It is shown that αγ-dichlorohydrin prepared as stated contains very little of the isomeric αβ-dichlorohydrin. The p-*nitrobenzoate* is prepared from samples boiling over a range of 3° and 7°, respectively. From 5 g. of chlorohydrin, the yields of ester are, respectively, 10·2 g. and 10·0 g., and the m. p. 55—58° and 53—57·5°. The pure ester has m. p. 58—59°. The p-*nitrobenzoate* of αβ-dichlorohydrin has m. p. 35·5—37°. A mixture of 90% of the αγ-ester and 10% of the isomeride melts between 26° and 48°. The crude products from the fractions above must contain less than 10% of the αβ-ester, and the original fractions must have contained at least 91% and 89% of αγ-dichlorohydrin, respectively. Probably the αβ-dichlorohydrin is almost completely absent. W. S. N.

Crystal Structure and Chemical Constitution of Basic Beryllium Acetate and Propionate. SIR W. BRAGG and G. T. MORGAN (*Proc. Roy. Soc.*, 1923, [*A*], **104**, 437—451).—Results obtained by Wyckoff (A., 1922, ii, 573), by W. L. Bragg (A., 1914, ii, 181), and by Clark (A., 1923, ii, 469), supporting Werner's theory of chemical combination and molecular structure based on the conception of co-ordination are briefly referred to. The physical and chemical properties of basic beryllium acetate do not support the formulation of this substance as a molecular compound, but indicate a unitary structure similar to that ascribed to non-ionised organic compounds. The preparation of basic beryllium acetate, m. p. 285—286°, of basic beryllium propionate, m. p. 133—135°, and of basic beryllium acetate-propionate, m. p. 140—142°, is briefly described. These m. p. values are in all cases higher, and in the case of the last two considerably higher (about 15°), than the highest respective values of the melting point recorded for these substances. Particulars of the determination, by *X*-ray analysis, of the respective crystal structures of basic beryllium acetate and propionate are given. The results support the formulation of the acetate group on a co-ordination basis, and confirm the validity of the structure of basic beryllium acetate suggested by Morgan and others, viz., the oxygen atom is situated at the centre of a tetrahedron, and the four beryllium atoms on the four lines joining the centre to the vertices, whilst the atoms composing an acetate group are disposed so as to be symmetrical about a plane perpendicular to each tetrahedron edge and passing through the opposite edge, *i.e.*, the six acetate groups span the edges of the tetrahedron. The crystal of basic beryllium propionate is, in accordance with anticipation, of lower symmetry, and is probably monoclinic prismatic with the following dimensions of the unit cell: *a*, 16·00 Å.; *b*, 9·76 Å.; *c*, 9·15 Å.; β, 116° 7′. Possibly the molecule of basic beryllium propionate, although approximately centrosymmetrical, has actually no symmetry at all. The crystal of basic beryllium acetate-propionate is not of high symmetry and is possibly analogous in structure to the propionate.

J. S. G. T.

The Acids in Beeswax. A. GASCARD and G. DAMOY (*Compt. rend.*, 1923, **177**, 1222—1224; cf. A., 1920, i, 418, 470).—Beeswax was saponified, and so converted into a mixture of acids. The mixture was fractionally crystallised from alcohol, using a method described previously (Gascard, *loc. cit.*). Four, and only four acids were present: *Neocerotic*, $C_{25}H_{50}O_2$ (m. p. 77·8°); cerotic, $C_{27}H_{54}O_2$ (m. p. 82·5°), identical with the acid from Chinese wax (Gascard, *loc. cit.*); montanic, $C_{29}H_{58}O_2$ (m. p. 86·8°) (cf. Tropsch and Kreutzer, A., 1922, i, 317, 804), and melissic, $C_{31}H_{62}O_2$ (m. p. 90°). E. E. T.

Preparation of Anhydrides of Fatty Acids of Low Molecular Weight. CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE (Brit. Pat. 194719).—Fatty acids of low molecular weight, particularly acetic acid, preferably diluted with inert gases or vapours, are led in rapid current over catalysts, such as the chlorides and sulphates of the alkalis and alkaline earths, boric acid, and borates, preferably mounted on porous carriers, at temperatures of about 400—700°. Yields of from 30—60% of acid anhydride are in this way readily obtained. The gases coming from the reaction chamber must be quickly cooled, and it is of advantage to inject into them liquids which have a cooling effect. Suitable liquids are those which are able to precipitate the water formed, and have a low boiling point, as, for instance, a volatile hydrocarbon. From the crude product pure anhydride may be obtained by adding a solvent, which precipitates most of the water, after which the solution of the anhydride is dried and separated from acid and solvent by fractionation. Propionic and butyric anhydrides may be prepared similarly. It is essential that any catalyst, such as alumina, which tends to promote the formation of ketones or of hydrocarbons should be absent from the reaction chamber.
T. S. W.

Addition to Compounds with Marked Conjugation. I. Addition of Hydrogen and Bromine to Sorbic Acid and Related Compounds. K. VON AUWERS and J. HEYNA (*Annalen*, 1923, **434**, 140—165; cf. this vol., i, 44).—The addition of bromine to sorbic acid (ester) and its homologues (prepared from unsaturated aldehydes and α-halogeno-esters) has been studied by effecting the ozonolysis of the resulting compounds, which are thus shown to be γδ-dibromides.

Sorbic acid forms a *p-toluidide*, m. p. 168—169°, and a *p-nitrobenzyl* ester, m. p. 70—72°. Dihydrosorbic acid (n_D^{20} 1·4393, d_4^{20} 0·965) forms an *anilide* (m. p. 54—56°) and a *p-bromophenacyl ether*, m. p. 63—65°. Sorbic acid dibromide, on ozonolysis, affords αβ-dibromobutaldehyde, which at once passes into α-bromocrotonaldehyde. [The semicarbazone decomposes at 162° (Viguier, A., 1913, i, 444, gives m. p. 228—230°). The phenylhydrazone has m. p. 117° (Viguier gives 125°).]

Bromoacetaldehyde is converted by semicarbazide into glyoxal disemicarbazone. α-Bromopropaldehyde with semicarbazide hydro-

chloride and sodium acetate gives either acetol-semicarbazone (m. p. 195°) or methylglyoxal disemicarbazone (m. p. 256°).

Ethyl sorbate with bromine gives *ethyl* γδ-*dibromo*-Δ$^{\alpha}$-*hexenoate*, yellow oil, b. p. 139°/11 mm. (with partial decomposition). The dibromo-ester affords the same products of ozonolysis as are given by the acid.

Ethyl crotonylidenemalonate, a yellow oil, b. p. 148—151°/15 mm., gives, with bromine, *ethyl* γδ-*dibromobutylidenemalonate* (yellow oil), this compound, when treated successively with ozone, etc., and a mixture of semicarbazide hydrochloride and sodium acetate, giving either *ethyl mesoxalate semicarbazone* (m. p. 55—56°), or the *compound*, $\begin{matrix}NH_2\cdot CO\cdot NH\cdot NH\\ HO\end{matrix}\!\!>\!C\!<\!\begin{matrix}CO_2Et\\ CO_2Na\end{matrix}$, m. p. 242°, the latter also being obtainable from ethyl mesoxalate and the above reagent.

α-Methylsorbic acid has m. p. 100—101° (Jaworsky and Reformatsky, A., 1903, i, 728, give 90—92°), forms an *ethyl* ester (a colourless oil, b. p. 207° or 100°/15 mm.), and on reduction gives α-*methyl*-Δ$^{\beta}$-*hexenoic acid*, b. p. 113·5°/15 mm., d_4^{20} 0·942, n_D^{20} 1·4395 (the latter giving a p-*bromophenacyl* ester, m. p. 41—42°, and a *dibromide*, m. p. 107—108°). α-*Methylsorbic acid dibromide*, needles, m. p. 114—115°, gives a yellow oily *ozonide*, which, on decomposition, affords α-bromocrotonaldehyde.

α-Ethylsorbic acid, needles, m. p. 85—86° (Jaworsky and Reformatsky give 75—77°) was obtained by the action of potassium hydrogen sulphate on *ethyl* p-*hydroxy*-α-*ethyl*-Δ$^{\gamma}$-*hexenoate* (produced by a Reformatsky reaction), gives an *ethyl* ester, b. p. 103—103·5°/13 mm., and on reduction affords α-*ethyl*-Δ$^{\beta}$-*hexenoic acid*, oil, b. p. 118—119°/12 mm., d_4^{20} 0·928, n_D^{20} 1·4421 (p-*bromophenacyl* ester has m. p. 34°). The latter acid forms a *dibromide*, needles, m. p. 118—119°, and on ozonolysis affords a mixture of propionic and butyric acids with the corresponding aldehydes.

α-Ethylsorbic acid with bromine gives γδ-*dibromo*-α-*ethyl*-Δ$^{\alpha}$-*hexenoic acid* (needles, m. p. 130·5—131·5°), the latter on ozonolysis being converted into α-bromocrotonaldehyde.

γ-Methylsorbic acid (from the action of potassium hydrogen sulphate, etc., on β-*hydroxy*-γ-*methyl*-Δ$^{\gamma}$-*hexenoic* ester, b. p. 112—120°/11 mm.), forms needles, m. p. 94—95° (*ethyl* ester, b. p. 98—99°/12 mm.), and on reduction affords γ-*methyl*-Δ$^{\beta}$-*hexenoic acid*, a mobile, colourless oil, m. p. 111° [sic., ? b. p. 111°/12 mm.], d_4^{20} 0·966, n_D^{20} 1·4503. The latter acid, with 2% permanganate solution is converted into acetic acid and methyl ethyl ketone.

βδ-Dimethylsorbic acid, on esterification, gives a mixture of *ethyl* ester (b. p. 87°/9 mm.) and a lactone (cf. Rupe, A., 1909, i, 927), whilst it forms a brown, oily *dibromide*, and on reduction affords βη-dimethyl-Δ$^{\beta}$-hexenoic acid, which has $n_D^{15\cdot8}$ 1·44800 and d_4^{20} 0·932. E. E. T.

Bismuth Oxalates. E. Moles and R. Portillo (*Anal. Fís. Quím.*, 1923, **21**, 401—408).—The preparation by different methods of normal bismuth oxalate, $Bi_2(C_2O_4)_3,7H_2O$, is described. On

heating at 130—150°, 6 mols. of water of crystallisation are lost. The salt thus obtained is red or pink and readily absorbs water, giving the salt with 7 mols. of water. Both salts give by hydrolysis an oxalate having the formula $[(BiO)HC_2O_4]_2,H_2O$, in which the water molecule is closely combined and is supposed to be attached to two bismuth atoms. G. W. R.

Salts of Maleic, Fumaric, and *i*-Malic Acids. J. M. Weiss and C. R. Downs (*J. Amer. Chem. Soc.*, 1923, **45**, 2341—2349).—A number of salts of the above-mentioned acids are described, of which some are new, whilst others have properties different from those described in the literature.

Strontium fumarate, dried at 100°, is anhydrous. *Calcium hydrogen fumarate*, air-dried, $+2H_2O$. Calcium hydrogen *i*-malate, air-dried, is anhydrous. Magnesium *i*-malate is not obtained crystalline. *Cobalt maleate*, $+11H_2O$; cobalt fumarate, air-dried, $+4H_2O$, dried at 100°, $+2H_2O$. *Cobalt* i-*malate*, $+3H_2O$. Nickel fumarate, $+4H_2O$ or $+5H_2O$; from concentrated solution, $+5H_2O$. *Nickel* i-*malate* is crystalline. *Manganous hydrogen maleate*, air-dried, $+4{\cdot}5H_2O$; *manganous maleate*, dried at 100°, $+3H_2O$; manganous fumarate, dried at room temperature, is anhydrous. Zinc fumarate, air-dried, $+5H_2O$. Ferric maleate, dried at 100°, a nearly black, amorphous mass, is evidently the dihydrate. *Ferric ammonium* i-*malate* resembles ferric ammonium citrate, but is less stable. Copper fumarate, dried at 100°, $+2H_2O$; *copper* i-*malate*, when air-dried, passes through the trihydrate to the dihydrate, but this result is not certain. *Cadmium fumarate*, dried at 100°, is anhydrous; *cadmium maleate*, air-dried, $+2H_2O$. A white, hard substance is described as *sodium antimonyl* i-*malate*. Lead fumarate, dried at 100°, is anhydrous, and so is lead maleate; lead *i*-malate softens at 100° to a dough-like mass, and is apparently the compound $PbC_4H_4O_5,\frac{1}{2}H_2O$. *Silver fumarate*, like silver maleate, deflagrates when heated. Other salts have been found to have the properties previously assigned to them. The solubilities in water of 22 salts are given. In general, fumarates are less soluble than the corresponding maleates. W. S. N.

Preparation of Methylglycuronide by the Oxidation of Methylglucoside. K. Smoleński (*Roczniki Chemji*, 1923, **3**, 153—164).—Glycuronic acid cannot be obtained by the direct oxidation of dextrose because the aldehyde group is the first to be attacked and gluconic acid (and saccharic acid) are produced. It was suggested by Fischer (A., 1891, 677) that glycuronic acid is produced in the animal organism by the oxidation of dextrose in which the aldehyde group is protected and it is now shown that this supposition is justifiable. The oxidation of α-methylglucoside by means of bromine and sodium carbonate or, better still, hydrogen peroxide with a trace of ferric hydroxide, leads to the formation of methylglycuronide, which is obtained in yields up to 30% and can be isolated in the form of its brucine salt. G. A. R. K.

Autoxidations. I. Autoxidation of Cysteine and Poisoning by Hydrocyanic Acid. E. ABDERHALDEN and E. WERTHEIMER (*Pflüger's Archiv*, 1923, **197**, 131—146; from *Chem. Zentr.*, 1923, iii, 463).—The autoxidation of cysteine is closely controlled by the reaction of the medium. An acid reaction depresses oxidation. Rapid oxidation occurs at litmus neutrality, whilst oxidation is appreciable with alkaline reaction. The temperature has an effect, since at 100° the nitroprusside reaction is no longer obtainable. Iron, copper, mercury, and arsenic favour oxidation, whilst lead, nickel, cobalt, uranium, thorium, and cadmium have no effect. Autoxidation is unaffected by light. In continuation of earlier experimental work on the effect of hydrocyanic acid (*Pflüger's Archiv*, 1922, **194**, 147), it was found that organs of animals poisoned by hydrocyanic acid retained the nitroprusside reaction twice as long as organs of normal animals. Potassium cyanide inhibits the autoxidation of cysteine. Alcohols, chloroform, and ethyl ether favour autoxidation. The reverse action, whereby the oxidised products are again reduced, was also studied. The thiol group of cysteine is again reduced by the tissues. It is supposed that in inhibition of autoxidation by hydrocyanic acid, the thio-group of the cysteine is the point of attack, and that cyanogen attached to the labile sulphur group reacts with oxygen. The normal reaction is represented by $R{\cdot}SH{\cdot}R \rightleftharpoons S{-}S{\cdot}R$, whilst in the presence of alcohols the reaction is $R{\cdot}SH{\cdot}R \rightarrow [R{\cdot}S{-}S{\cdot}R]$, and is irreversible. In the presence of hydrocyanic acid, the reverse reaction follows the course $R{\cdot}S{-}S{\cdot}R \rightarrow R{\cdot}SH + SS{\cdot}R$.

G. W. R.

Autoxidations. II. The Transformation of Cysteine into Cystine. E. ABDERHALDEN and E. WERTHEIMER (*Pflüger's Archiv*, 1923, **198**, 122—127; from *Chem. Zentr.*, 1923, iii, **463**; cf. preceding abstract).—The autoxidation of cysteine and also the inhibition of the reaction by hydrocyanic acid can take place in the absence of iron. Oxidation of cysteine is, however, accelerated by the addition of small quantities of ferric chloride solution. In this case, the iron acts simply as a catalyst. This is in contradiction to Warburg's view (A., 1922, i, 190), that iron plays an essential part in the autoxidation of cysteine. G. W. R.

Autoxidations. III. E. ABDERHALDEN and E. WERTHEIMER (*Pflüger's Archiv*, 1923, **198**, 415—420; from *Chem. Zentr.*, 1923, iii, 690; cf. preceding abstracts).—In the reactions alcohol $\rightleftharpoons$ aldehyde $\rightleftharpoons$ acid, the presence of cystine favours the formation of acid whilst cysteine favours the formation of alcohol. The change from cysteine to cystine is more rapid than the reduction of cystine so that an excess of cystine is soon present which reverses the effect of the cystine originally present. The reversible change cysteine $\rightleftharpoons$ cystine has an important effect on oxidations and reductions in cells, and serious disturbances are produced if this balance is destroyed as in dystrophy and hydrocyanic acid poisoning. The equilibrium between β-hydroxybutyric acid and acetoacetic acid is also influenced by the cysteine–cystine system. G. W. R.

The so-called Auto-oxidation of Cysteine. S. SAKUMA (*Biochem. Z.*, 1923, **142**, 68—78).—Cysteine prepared by the reduction of cystine by the Baumann and Friedmann methods, carefully purified by treatment with barium hydroxide and hydrogen sulphide, and recrystallised as the hydrochloride from ethyl or propyl alcohol, using quartz or porcelain vessels in place of glass, is oxidised 100 to 250 times more slowly at a p_H 7·7 than cysteine preparations previously mentioned in the literature. The author's preparation showed $[\alpha]_D$ −228°. The auto-oxidation of cysteine is therefore ascribed to a catalytic oxidation caused by an impurity (probably metallic) which, in the case of the author's crude preparations, was iron. By the increased rate of oxidation of a highly purified cysteine traces of iron, not detectable by ordinary analytical methods, may be revealed. The inhibition of cysteine oxidation by cyanides is ascribed to their action on the metallic impurity and not on the cysteine itself. Pyrophosphates have a similar inhibiting influence. J. P.

α-Vinylcrotonaldehyde and, presumably, Sorbic Aldehyde [$\Delta^{\alpha\gamma}$-Hexadienaldehyde] from Acetaldehyde. S. ZEISEL and M. NEUWIRTH (*Annalen*, 1923, **433**, 121—138).—Zeisel and von Bittó (A., 1908, i, 761) obtained two doubly-unsaturated, open-chain aldehydes, having b. p. 55—60°/24—26 mm., and 75—80°/24—26 mm., respectively, by the auto-condensation of acetaldehyde by means of sodium acetate. These are now shown to be *α-vinylcrotonaldehyde* and $\Delta^{\alpha\gamma}$-hexadienaldehyde, respectively, by reducing the product of the reaction by means of fine iron wire and 50% acetic acid containing nickel acetate; the reaction is allowed to proceed for four days at the ordinary temperature, but is finally completed at 100°. α-Ethylbutaldehyde and *n*-hexan-α-ol are produced, together with small quantities of normal, unsaturated 6-carbon alcohols. The aldehyde is recognised by oxidation to α-ethylbutyric acid, by means of cold, aqueous chromic acid solution. The mixture of hexanol and its unsaturated analogue is further reduced by the action of hydrogen in the presence of a nickel catalyst at 175—230°, and *n*-hexan-α-ol, b. p. 150—157°, is isolated from the product; it is recognised by oxidising it to *n*-hexoic acid by means of boiling, aqueous chromic acid solution.

The formation of $\Delta^{\alpha\gamma}$-hexadienaldehyde may occur by the condensation of the methyl group of acetaldehyde with the aldehyde radicle of crotonaldehyde, or, conversely, condensation may occur between the methyl group of crotonaldehyde and the aldehyde group of acetaldehyde; either reaction will be followed by the elimination of water. Or aldol, rather than crotonaldehyde, may react with acetaldehyde, 2 mols. of water being subsequently removed. For production of α-vinylcrotonaldehyde there is, however, only one feasible explanation; condensation takes place between the aldehyde group of acetaldehyde and the methylene radicle of aldol, 2 mols. of water being then eliminated:

$$OH\cdot CHMe\cdot CH_2\cdot CHO + CHO\cdot Me \longrightarrow OH\cdot CHMe\cdot CH(CHO)\cdot CHMe\cdot OH \longrightarrow CHMe{:}C(CH{:}CH_2)\cdot CHO + 2H_2O.$$

W. S. N.

Hydrogenation of certain Ketones in Presence of Pure or Impure Platinum Black. M. FAILLEBIN (*Compt. rend.*, 1923, **177**, 1118—1120).—It was previously shown (A., 1923, i, 92) that better yields of alcohols were obtained by the hydrogenation of ketones and aldehydes in presence of platinum black containing iron than in presence of pure platinum black. It is now found that ethyl acetoacetate, on hydrogenation using pure platinum black, gives ethyl butyrate, whereas, if the black contains iron, almost pure ethyl β-hydroxybutyrate results. This ester is not hydrogenated in presence of pure platinum, so that the two different results must be due to two distinct processes.

Aluminium gives results similar to those obtained with iron, in the cases of ethyl acetoacetate and benzaldehyde, whilst with δ-*p*-methoxyphenyl-β-butanone a 50% conversion into alcohol occurs, whereas in the absence of aluminium platinum black gives no alcohol.

Platinum black containing colloidal silica (obtained by adding a solution of sodium silicate in hydrochloric acid to chloroplatinic acid, etc.) allows of the conversion of ethyl acetoacetate into hydroxy-ester, but in the case of most aldehydes and ketones behaves like pure platinum.

The decisive nature of the results obtained with ethyl acetoacetate could be attributed to the production and reduction of the enolic form of the ester. On the other hand, the pure enolic form could not be hydrogenated, using pure platinum black, to give the hydroxy-ester, although it was shown that the catalyst does not convert the enolic into the ketonic form. Similarly, the use of solvents in which the ester is known to exist mainly as enol led to no better results.

With acetylacetone (which contains 80% of the enolic form), the iron–platinum catalyst gave a mixture of the ketone-alcohol and the dihydroxy-compound, whereas, with a platinum catalyst, methyl *n*-propyl ketone and *n*-pentane were obtained. The effects described may be due to the formation of complex iron or aluminium compounds with enolic forms, but iron and aluminium acetylacetonates and the copper derivative of ethyl acetoacetate are not hydrogenated using pure platinum black. Again, the metal hydroxides may stabilise the enolic form (cf. also, Carothers and Adam, A., 1923, ii, 310). E. E. T.

Galactose Sulphuric Acid. S. AKAMATSU (*Biochem. Z.*, 1923, **142**, 181—183).—By the action of chlorosulphonic acid in chloroform on dry galactose a pasty product was obtained, which, when treated with ice-cold barium hydroxide solution and repeatedly precipitated from aqueous solution by the addition of alcohol, yielded *barium galactose tetrasulphate*, $C_6H_8O_6(SO_3)_4Ba_2,3H_2O$, as a colourless powder, readily soluble in water, and capable of reducing boiling Fehling's solution. The barium salt was not fermented by yeast or by sulphatase (A., 1923, i, 1148). It began to decompose at 60°. By the action of potassium carbonate solution it was converted to the normal *potassium* salt, $C_6H_8O_6(SO_3)_4K_4$, which gave

no precipitate with barium chloride, decomposed at 200°, and had $[\alpha]_D^{20}$ +41·7° (c=2·443). J. P.

Position of the Point of Pseudo-transition of Dextrose: $S_{aq} \rightleftharpoons S^a + L$ (in Internal Equilibrium). J. GILLIS (*Rec. trav. chim.*, 1923, **42**, 1077—1079).—The author, using figures obtained by Jackson and Silsbee (A., 1922, i, 986) for the solubility of dextrose in water, has plotted the reciprocal of the temperature against log x, where $x=gM^{-1}/(gM^{-1}+100M_1^{-1})$, M and M_1 being the mol. weights of dextrose and water, respectively, and g the weight of anhydrous dextrose contained in 100 g. of water at different temperatures. The curve so obtained, however, does not permit of the determination of the temperature of pseudo-transition, as it might be expected to. The author thinks that this temperature is slightly higher than 50°, the experimental figure of Jackson and Silsbee. E. E. T.

The Preparation of Di*iso*propylidene Glucose. P. A. LEVENE and G. M. MEYER (*J. Biol. Chem.*, 1923, **57**, 317—318).—Using Fischer and Rund's method (A., 1916, i, 363), di*iso*propylidene glucose may be prepared from dextrose (α-glucose) and commercial acetone, although the yields are smaller than when β-glucose and dry acetone are employed. An economy of time is effected by using the former method. E. S.

Benzylidene *iso*Propylidene Glucose. P. A. LEVENE and G. M. MEYER (*J. Biol. Chem.*, 1923, **57**, 319—322).—When benzylidene *iso*propylidene glucose is methylated with methyl sulphate and sodium hydroxide, and the product so obtained is hydrolysed with hydrochloric acid, a methyl glucose, m. p. 156—157°, $[\alpha]_D^{20}$ +103° (initial), +57° (final) (in water), is obtained. Oxidation of the methyl glucose with nitric acid yields a methyl saccharolactone. In both cases, the products are identical with those obtained from di*iso*propylidene glucose (A., 1923, i, 92). Further, benzoylation of benzylidene *iso*propylidene glucose yields a benzoyl *iso*propylidene glucose identical with that obtained from di*iso*propylidene glucose. It is concluded that benzylidene *iso*propylidene glucose and di*iso*propylidene glucose have analogous structures and that accordingly the former is εζ-benzylidene αβ-*iso*propylidene glucose. E. S.

The Allyl Ethers of Various Carbohydrates. C. G. TOMECKO and R. ADAMS (*J. Amer. Chem. Soc.*, 1923, **45**, 2698—2701).—Various carbohydrates are treated with allyl bromide in the presence of 10% sodium hydroxide solution; the following allyl ethers are obtained. *α-Methyltetra-allylglucoside*, a thick, colourless oil, b. p. 182°/1·5 mm., n_D^{18} 1·4836, d_{20}^{20} 1·1519, $[\alpha]_D^{30}$ +116·5° (in alcohol). *Penta-allyl sucrose*, a thick, almost colourless oil. *Allyl dextrin*, *allyl inulin*, *allyl potato starch*, and *allyl maize starch* are white amorphous solids, which, when heated, behave respectively as follows: shrinks at 155—165° and gradually decomposes at about 240—250°; shrinks at 150—155° and decomposes at 205—210°; shrinks at 160—165° and decomposes without melting at 260—

270°; and becomes brown at 250—265°, but does not shrink or melt. *Allylated cellulose* has been prepared. W. S. N.

Some Glucosides and Galactosides of Thiols. E. Potel (*Bull. Soc. chim.*, 1923, **33**, [iv], 1459—1465).—The method of preparation in each case consisted in condensation of the sugar with the thiol by means of hydrochloric acid in concentrated solution. The following are described: glucose *n*-propyl mercaptal (cf. Schneider, Sepp, and Stiehler, A., 1918, i, 252); *galactose* n-*propyl mercaptal*, long, white needles, m. p. 130—131°; *glucose* n-*butyl mercaptal*, white needles, m. p. 124—125°, slight decomp. at the ordinary temperature; *galactose* n-*butyl mercaptal*, white needles, m. p. 122—123°; *glucose* n-*heptyl mercaptal*, a white, crystalline powder, m. p. 116—118°; *galactose* n-*heptyl mercaptal*, pearly crystals, m. p. 113—115°. The condensation appears to become more difficult with increasing number of carbon atoms in the thiol employed. Galactose combines more readily than glucose. All the above substances are hydrolysed on heating with dilute acids, regenerating thiol and hexose. H. J. E.

Preparation of α-Mannose. P. A. Levene (*J. Biol. Chem.*, 1923, **57**, 329—336).—α-Mannose, m. p. (decomp.) 205° after becoming a semi-solid mass at 133° (corr.), $[\alpha]_D^{20}$ +30° (in water), +35° (in 80% alcohol), has been prepared from β-mannose, (*a*) by dissolving in pyridine and precipitating with alcohol, (*b*) by dissolving in hot water and precipitating with glacial acetic acid at 0°, and (*c*) by dissolving in concentrated ammonia and precipitating with ether after the addition of alcohol. The first two methods are those used for the preparation of β-glucose and β-galactose; the third method also forms a convenient method for the preparation of these substances. Mannose thus crystallises in the α-form under conditions in which β-glucose and β-galactose appear. The specific rotation of α-mannose agrees with that calculated by Hudson and Yanovsky (A., 1917, i, 445), but the sum of the constants k_1+k_2 in the equation of Hudson (A., 1904, i, 974) and of Lowry (T., 1904, **85**, 1551) has a different value when measured on the α-form than when obtained from the β-isomeride. It is thus possible that the α-isomeride contains a third form of mannose. E. S.

Action of Chloral on Cellulose. J. H. Ross and J. M. Payne (*J. Amer. Chem. Soc.*, 1923, **45**, 2363—2366).—When cotton cellulose is treated with chloral hydrate in the presence of an excess of cold, concentrated sulphuric acid, chloral-substituted celluloses or cellulose dextrins are not obtained. Instead, four substances are formed. (*a*) Triangular or hexagonal plates, m. p. 268° (*monoacetate*, m. p. 198°, $[\alpha]_D$ −12° in chloroform solution, *methyl ether*, ciliate needles, m. p. about 200°, $[\alpha]_D$ −17° in acetone–pyridine solution), which is lævorotatory and is evidently identical with Pictet and Reichel's *iso*dichloralglucose-*A* (A., 1923, i, 755). (*b*) Needles, m. p. 225°, $[\alpha]_D$ −15° in chloroform solution (*acetate*, thick, rectangular crystals, m. p. 126°, $[\alpha]_D$ −21·4° in chloroform solution, very soluble *methyl ether*, m. p. about 110°, $[\alpha]_D$ −23° in

chloroform solution), which is apparently identical with Meunier's dichloralglucose (A., 1896, i, 334). (*c*) Long needles, m. p. 135—136°, $[\alpha]_D$ +32° in benzene, +10·5° in chloroform solution. (*d*) A syrup solidifying on cooling, m. p. about 74—75°, $[\alpha]_D$ +14° in chloroform solution, which seems to contain some of (*b*). The substances (*c*) and (*d*) are evidently dichloralglucoses; they do not give crystalline acetates or methyl ethers. The same four substances are produced in a similar manner from hydrocellulose, starch, or glucose. In addition to the compounds (*a*), (*b*), (*c*), and (*d*), parachloralose is formed in every case. Since it is claimed by previous workers (Pictet and Reichel, *loc. cit.*) that this substance is produced by the α-anhydroglucosidic linking of *d*-glucosan, but not by the β-anhydroglucosidic linking of *l*-glucosan, its formation from cellulose may indicate the presence of one or more α-linkings in the cellulose molecule. W. S. N.

Cellulose Chemistry. IV. Properties of γδ-Dihydroxycarbonyl Derivatives and their Bearing on the Polymerisation of Polysaccharides. H. Hibbert and J. A. Timm (*J. Amer. Chem. Soc.*, 1923, **45**, 2433—2439).—Methyl γδ-dihydroxybutyl ketone, $OH{\cdot}CH_2{\cdot}CH(OH){\cdot}[CH_2]_2{\cdot}COMe$, b. p. 158—160°/7—8 mm. (Traube and Lehmann, A., 1901, i, 501), undergoes dehydration and resinification when heated at 120—130° in the presence of a trace of concentrated sulphuric acid; analysis of the resin, and the direct weighing of the water evolved, show that 1 mol. of water is evolved for every molecule of hydroxy-ketone. This is not due to the primary formation of an ethylene oxide ring,

$$\begin{matrix} CH_2 \\ | \\ O\text{—} \end{matrix}\!\!>\!CH{\cdot}[CH_2]_2{\cdot}COMe\ (I),$$

and subsequent polymerisation, because the substance (I) is known (γ-ketobutylethylene oxide, Kablukow, A., 1888, 1171), and does not undergo polymerisation under the same conditions, although charring occurs after long heating. The explanation favoured is that the elimination of water takes place from the butylene oxide form of the ketone, giving the unsaturated radicle,

$$-O{\cdot}CH_2{\cdot}\underset{\llcorner\!\!-\!O\!-\!\!\lrcorner}{CH}{\cdot}[CH_2]_2{\cdot}CMe-,$$

which then undergoes polymerisation to give a substance the structure of which is analogous to that advocated for cellulose (*J. Ind. Eng. Chem.*, 1921, **13**, 256, 334). Experiments are in progress which should show whether the ketone contains the butylene oxide, or the alternative amylene oxide, ring. W. S. N.

Researches on Pectins. K. Smoleński (*Roczniki Chemji*, 1923, **3**, 86—152).—It has already been shown by the author that the pectin of the sugar-beet contains the glycuronic acid residue (A., 1911, ii, 428), and later (*Proceedings* of the 2nd Mendeléev Congress, 1911, 45) it was suggested that glycuronic acid is the intermediate product in the formation of pentoses from hexoses. The work on these substances has now been extended.

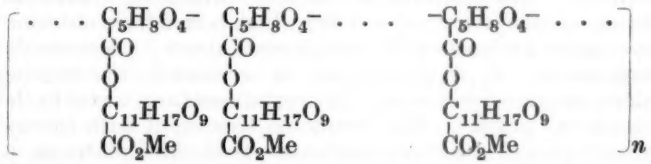
I. [With Mme E. Smoleńska.]—The method of preparation of pectin from sugar-beet residues has been improved. The best

yields are obtained by using dilute mineral acids; the use of alkalis leads to products with a low viscosity in solution, this property being used as a criterion of purity. From the crude material so obtained alcohol precipitates a dry white powder which dissolves in water to give solutions many times more viscous than those of gum arabic; it does not reduce Fehling's solution, gives the naphtharesorcinol test for glycuronic acid, and a yellow coloration with sodium hydroxide.

The action of 1% sulphuric acid on the purified pectin (previously treated with sodium hydroxide) at 125—130° in an autoclave leads to glycuronic acid which reduces Fehling's solution and gives the naphtharesorcinol reaction.

II. [With Mme A. Komornicka and W. Stypiński.]—The crude pectin from sugar-beet residues can be divided into two substances by adding alcohol to its aqueous solution; about 60% of the material is insoluble in 75% alcohol. The insoluble portion, or "purified pectin," is found to contain *d*-galacturonic acid in considerable amount, whilst the alcohol-soluble portion is a polysaccharide consisting almost entirely of *l*-arabinose residues; this "araban" is lævorotatory and readily undergoes hydrolysis, after which the sign of rotation changes. It is suggested that the original pectin of the sugar-beet is insoluble in water and passes into solution as the result of hydrolysis; this process proceeds rapidly in the presence of $1/200N$-mineral acid.

The hydrolysis of purified pectin by means of a slight excess of alkali was studied and was found to be complete after two to three hours at 20° or a few minutes at 75°. Methyl alcohol was found in the hydrolysis product (cf. Fellenberg, A., 1917, i, 616; 1918, i, 215). From a consideration of these and other authors' data a possible constitutional formula is suggested:



in which galacturonic acid is combined by means of its carboxyl group with the methyl ester of galacto-galacturonic acid. In the original insoluble pectin pentoxide, complexes are also present, in addition to which the existence of gluco-glycuronic complexes is probable. These and the galacto-galacturonic complexes probably form transition stages between hexoside and pentoside complexes; these substances are presumably oxidation products of hexosans such as the starches. G. A. R. K.

The Biuret Reaction. L. Hougounenq, G. Florence, and E. Couture (*Bull. Soc. Chim. biol.*, 1923, **5**, 717—721).—On heating in a sealed tube at 180° acetylglycine and aniline, there was obtained a mixture of acetylglycylanilide, m. p. 196°, and acetyldiglycylanilide, m. p. 246°. The latter gives the ordinary biuret reaction; the

former an emerald-green colour. The green compound was isolated and its analysis corresponds with the composition

$$3C_{10}H_{12}O_2N_2,3Cu(OH)_2,4KOH,6H_2O.$$

Benzoylglycylanilide was the only other compound found to give a green colour with copper sulphate and potassium hydroxide.

C. R. H.

Reactions of Peptide-like Compounds. II. Derivatives of γ-Amino-β-hydroxybutyric Acid. M. BERGMANN, E. BRAND, and F. WEINMANN (*Z. physiol. Chem.*, 1923, **131**, 1—17).—Potassium cyanide reacts with γ-benzamido-β-hydroxypropyl chloride to form *γ-benzamido-β-hydroxybutyronitrile*, long, crossed plates, m. p. 128—129° (corr.). Treatment of this cyanide with alcoholic hydrogen chloride results in the formation of the *imino-ether hydrochloride*, a colourless, crystalline powder, which is readily hydrolysed to *ethyl γ-benzamido-β-hydroxybutyrate*, m. p. 99—100°, and from this, *γ-benzamido-β-hydroxybutyric acid*, fine needles, m. p. 176—177° (corr.), is easily obtained. By the action of thionyl chloride ring formation occurs, and when the acid chloride m. p. 117—118° (corr. decomp.) formed is decomposed by water, it yields the free acid *2-phenyloxazoline-5-acetic acid*, m. p. 140—141° [*hydrochloride*, m. p. 179° (decomp.)]. The hydrochloride of the cyclic oxazoline compound, when allowed to remain for two hours in aqueous solution, is converted into *γ-amino-β-benzoxybutyric acid* [*hydrochloride*, needles, m. p. 215° (decomp.)]. In a similar way, thionyl chloride converts ethyl γ-benzamido-β-hydroxybutyrate into *ethyl 2-phenyloxazoline-5-acetate*, a thick oil, b. p. 180°/1·5 mm., $n_D^{19\cdot9}$ 1·5283 (*hydrochloride*, needles, m. p. 118—119° corr.), whilst this compound is converted by the action of 2*N*-hydrochloric acid into a *compound*,

$$C_{11}H_{17}O_6N,HCl,$$

fine, filamentous, white needles, m. p. 205°, which on treatment with alkali forms a *compound*, m. p. 175°, which is free from chlorine.

From the imino-hydrochloride mentioned above, *γ-benzamido-β-hydroxybutyramide*, $C_{11}H_{14}O_3N_2,H_2O$, is obtained by heating at 130° under a pressure of 10 mm. It crystallises from water in the form of prisms, m. p. 130°. This amide on treatment with thionyl chloride forms *2-phenyloxazoline-5-acetamide*, 4—6-sided plates, m. p. 168° (corr.) (*picrate*, citron-yellow crystals, m. p. 156—157° corr.). In acid solution, one nitrogen atom is eliminated from this oxazoline compound, and a strongly reducing substance is formed. The amide may also be conveniently prepared by the action of ammonia on the acid chloride formed from γ-benzamido-β-hydroxybutyric acid. γ-Amino-β-hydroxybutyric acid is obtained by hydrolysing ethyl γ-benzamido-β-hydroxybutyrate with hydrobromic acid (48%), and may be isolated as the *hydrobromide*, $C_4H_9O_3N,HBr$, long needles, m. p. 78°, whilst the free acid, m. p. 218°, is obtained if the hydrolysis is carried out with sulphuric acid, and the sulphuric acid is removed as barium sulphate. When the acid is heated with zinc dust, the fumes give an intense pyrrole reaction with a pine shaving. γ-Amino-β-hydroxybutyric acid has been previously described by Tomita (A., 1923, i, 190).

W. O. K.

Formaldehyde Compounds of Simple Amino-acids. M. BERGMANN, M. JACOBSOHN, and H. SCHOTTE (*Z. physiol. Chem.*, 1923, **131**, 18—28).—By the action of a strong solution of formaldehyde on ethyl glycollate hydrochloride, and subsequent liberation of the base with alkali, a *triformaldehyde-glycine* ester, $C_3H_6O_2{:}N{\cdot}CH_2{\cdot}CO_2Et$, is obtained. It is a colourless liquid which may be distilled under 1 mm. pressure from a bath at 98—100°. It loses formaldehyde easily on boiling with water, and particularly easily on treatment with acid or alkali. Treatment with barium hydroxide solution results in the formation of the *barium* salt of *methyleneglycine*, $(CH_2{:}N{\cdot}CH_2{\cdot}CO_2)_2Ba,5H_2O$, colourless needles or prisms. This compound may also be produced by the action of formaldehyde on glycine in presence of baryta. Treatment of triformaldehydeglycine ester with ammonia yields *triformaldehydeglycinamide*, $C_3H_6O_2{:}N{\cdot}CH_2{\cdot}CO{\cdot}NH_2$, glistening leaflets, m. p. 140°. Triformaldehyde-γ-amino-αβ-dihydroxypropane is obtained by the action of formaldehyde on γ-amino-αβ-dihydroxypropane, and is a syrup, b. p. 120—150°/0·3 mm.; with picric acid, this compound loses formaldehyde and forms a *picrate*, $C_{10}H_{12}O_9N_4$, flat, yellow, microscopic needles, m. p. 143—144°, and similarly with oxalic acid an *oxalate* is formed. The hydrochloride of the ethyl ester of serine forms a similar triformaldehyde *compound*, $C_9H_{17}O_5N$, an oil, b. p. 76—78°/0·7 mm. W. O. K.

Epichitosamine Penta-acetate. P. A. LEVENE (*J. Biol. Chem.*, 1923, **57**, 323—327).—Some anomalies are pointed out in connexion with the conclusion of Irvine and Earl (T., 1922, **121**, 2370) that chitosamine has the configuration of dextrose. On the basis of this conclusion, epichitosamine (A., 1919, i, 475) should have the configuration of mannose. On the other hand, from the fact that epichitose is β-ε-anhydrodextrose it would appear that epichitosamine had the configuration of dextrose. Further, when the rotation of the β-carbon atom in the epimeric amino-sugars is calculated from their molecular rotations, it is found to rotate to the left in epichitosamine and to the right in chitosamine; in the corresponding acids, however, the direction of the rotation of the same carbon atom is reversed. This is apparently due to differences produced in the structure of the α-carbon atom by oxidation.

β-*Epichitosamine penta-acetate*, $C_8H_8O_5N(CH_3{\cdot}CO)_5$, long needles, m. p. 158—159° (corr.), $[\alpha]_D^{20}$ −18° (in chloroform), has been prepared by treating epichitosamine hydrochloride with acetic anhydride and pyridine. When heated with zinc chloride in acetic anhydride solution, it is converted into the α-isomeride. E. S.

The Two Isomeric Chondrosamine Hydrochlorides and the Rates of their Mutarotation. P. A. LEVENE (*J. Biol. Chem.*, 1923, **57**, 337—340).—The two isomeric chondrosamine hydrochlorides have been prepared. The β-form had $[\alpha]_D^{20}$ +47°, although the extrapolated value obtained from the rate of mutarotation was $[\alpha]_D^{20}$ +44·5°; the α-form had $[\alpha]_D^{20}$ +121°. The difference between

the molecular rotations of the two forms is 16,485 and is thus practically the same as the usual value for other sugars. E. S.

The Iron–Cyanogen Compounds. M. KOHN and L. BENCZER (*Monatsh.*, 1923, **44**, 97—102).—The solubility of Prussian blue in solutions of the alkali metal oxalates (Kohn, A., 1923, i, 312) is due to the formation of the alkali metal ferrocyanide and the double ferric oxalate, in accordance with the equation $Fe_4[Fe(CN)_6]_3+8K_2C_2O_4=3K_4Fe(CN)_6+4KFe(C_2O_4)_2$. Most of the Prussian blue separates again slowly after acidification. Turnbull's blue is also soluble in the normal oxalates, forming potassium ferricyanide and potassium ferrous oxalate, which react to form the ferrocyanide and the double ferric oxalate; addition of acid to the solution precipitates Prussian blue. Ferrous ferrocyanide, obtained as a white precipitate by the addition of ferrous sulphate to potassium ferrocyanide, or to the solution of Prussian blue in the alkali oxalates, dissolves slowly in the oxalate solution with atmospheric oxidation. S. I. L.

Reaction between Magnesium and Calcium Salts and Rubidium and Cæsium Salts. E. MURMANN (*Oesterr. Chem. Ztg.*, 1923, **26**, 140—141).—When a very dilute solution containing calcium chloride and potassium ferrocyanide is heated at 50° and mixed with a dilute solution of a rubidium or cæsium salt, a precipitate forms which may be collected and washed with 60% alcohol until free from chlorides. In the case of calcium and cæsium, the precipitate, after being dried at the ordinary temperature, has a composition corresponding approximately with the formula $Cs_4Ca_2Fe_2(CN)_{12},H_2O$. Similar compounds are formed when magnesium chloride is used in place of calcium chloride and potassium ferricyanide in place of potassium ferrocyanide. W. P. S.

Complex Compounds of Cobalt with Dimethylglyoxime. F. FEIGL and H. RUBINSTEIN (*Annalen*, 1923, **433**, 183—190).—Experiments have been made to determine the constitution of the brown compound (Tschugaev, A., 1905, i, 743) formed by the action of dimethylglyoxime on a solution containing cobalt-ions.

The action of dimethylglyoxime on cobaltous chloride in hot, concentrated aqueous-alcoholic solution, or, better, in boiling acetone solution, gives *cobaltobisdimethylglyoxime chloride*,

$$[Co(DH_2)_2]Cl_2$$

(DH_2=dimethylglyoxime), green crystals. This compound is converted by means of fuming hydrobromic acid in alcoholic solution into *cobaltobisdimethylglyoxime bromide*, green crystals. Both the chloride and the bromide have an intensely sweet taste. The bromide undergoes hydrolysis when boiled with water, giving *cobaltobisdimethylglyoxime bromide hydroxide*, $[Co(DH_2)_2](OH)Br$, yellowish-brown crystals; the reverse reaction is brought about by the action of concentrated hydrobromic acid. The bromide is converted by the action of aqueous-alcoholic ammonia into *cobaltoaquoamminobisdimethylglyoxime bromide hydroxide*,

$$[Co(NH_3)(H_2O)(DH_2)_2](OH)Br,$$

yellowish-brown crystals (blackish-brown, crystalline *periodide*).

The action of dimethylglyoxime on Naumann's compound, $CoCl_2,2NH_3$, in warm acetone solution gives *diamminocobaltobis-dimethylglyoxime chloride*, $[Co(NH_3)_2(DH_2)_2]Cl_2$, yellow crystals, together with the compound $[Co(DH_2)_2]Cl_2$. Evidently, besides the simple addition of two glyoxime molecules to the complex $CoCl_2,2NH_3$, substitution of the two NH_3 molecules by one glyoxime molecule, followed by addition of a second oxime molecule, also occurs. This process takes place exclusively when dimethylglyoxime reacts in boiling acetone solution with the compound $CoCl_2,2NH_2{\cdot}OH$ (Feldt, A., 1894, ii, 187), the sole product being the compound $[Co(NH_3)_2]Cl_2$. The prolonged action of dimethylglyoxime, in boiling solution, on the compound $CoCl_2,2NH_3$ leads to the formation of an insoluble, glistening, crystalline, ruby-red compound of unknown constitution. When cobaltous hydroxide and dimethylglyoxime are boiled in alcoholic solution, a brown solution is obtained from which a black *compound*, possibly cobaltibisdimethylglyoxime hydroxide, $Co(OH)_3,2DH_2$, is isolated.

The action of ammonia on the bromide (above) causes, therefore, an increase from four to six in the co-ordination number of the cobalt atom, which, however, remains bivalent. Tschugaev, on the other hand, obtained complexes containing tervalent cobalt, by the use of strongly basic substances (A., 1906, i, 814). In the experiments described above, however, ammonia is allowed to react with a substance already containing bivalent cobalt, whereas, in Tschugaev's experiments, dimethylglyoxime was caused to react with cobaltammine complexes in which a tervalent cobalt atom was already present. The formation of an additive compound from dimethylglyoxime and the compound $CoCl_2,2NH_3$, whilst with the compound $CoCl_2,2NH_2{\cdot}OH$ the simple chloride, $[Co(DH_2)_2]Cl_2$, is formed, certainly proves that the cobalt atom is bivalent in the simpler compounds described. W. S. N.

The Constitution of the so-called β-Dimethyl*iso*thiohydantoin. W. Wüdich (*Monatsh.*, 1923, **44**, 83—90).—The constitution of the substance obtained by Andreasch (A., 1888, 47) by the action of methyl iodide on the silver compound of *iso*thiohydantoin has been further examined. The silver compound contains two atoms of silver in the molecule, but is too unstable for analysis, decomposing even on long washing. The yield of the dimethyl compound is poor, amounting only to 11% of the theoretical; it has m. p. 174° (not 114° as given by Andreasch), and the formula is not $C_5H_8ON_2S$, but $C_5H_{10}O_2N_2S$.

By heating with hydrochloric acid in a sealed tube at 150°, and neutralising the product with barium hydroxide, barium methylthiolacetate $(SMe{\cdot}CH_2{\cdot}CO_2)_2Ba$, was obtained. The formation of the dimethyl compound is therefore accompanied by disruption the thiazole ring, $S<\begin{matrix}CH_2{\cdot}CO\\C(NH)-\end{matrix}>NH \rightarrow SMe{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C(NH){\cdot}OMe$, and the silver compound must have the formula

$$SAg{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C(NH){\cdot}OAg.$$

This constitution of the dimethyl compound, namely, methyl-

thiolacetyl*iso*methylcarbamide, was confirmed by Kirpal and Bühn's modification of Zeisel's method for the estimation of methoxyl groups (A., 1914, ii, 497), it being established by a blank determination with synthetic barium methylthiolacetate that the group SMe· does not yield methyl iodide under these conditions.

The corresponding *ethyl* compound, $C_7H_{14}O_2N_2S$, white needles, m. p. 156°, and benzyl compound, $C_{17}H_{18}O_2N_2S$, m. p. 183°, were prepared.

By treatment of *iso*thiohydantoin in aqueous solution with ammoniacal lead acetate, a lead salt, $C_3H_4O_2N_2SPb$, was obtained, thus confirming the formula suggested for the silver compound.

S. I. L.

Preparation and Detonating Qualities of Cyanuric Triazide. C. A. Taylor and W. H. Rinkenbach (*U.S. Bur. Mines, Repts. Investigations*, 1923, No. 2513).—Cyanuric triazide, $(CN)_3N_9$, white crystals, m. p. 94°, was prepared in 90% yield by the action of an aqueous solution of sodium azide on cyanuric chloride (prepared in 95% yield by James's method); the substance detonates when heated quickly. Small crystals are more sensitive to impact and friction than mercury fulminate; large crystals detonate when broken. In the molten state it is very sensitive to friction. It is non-irritating to the skin, and is non-poisonous in fairly large doses to rats and guinea-pigs, but the materials used in its preparation are irritating and poisonous. Chemical Abstracts.

Ring Closure with Hydrazinedicarbonamides containing Sulphur. IV. The Mechanism of Intramolecular Displacement. F. Arndt and F. Bielich (*Ber.*, 1923, **56**, [*B*], 2276—2283; cf. A., 1921, i, 813; 1922, i, 375; 1923, i, 611).—The author has previously expressed the view that, in the formation of cyclic compounds from hydrazinedicarbonamides containing sulphur, the most basic product (thiodiazole) is formed in an acid medium, whereas the most acidic product (triazole) is produced in the presence of bases. This rule is now found to require modification. The whole investigation points to the conclusion that intramolecular displacements are the result of two reactions consisting of first an elimination (of hydrogen sulphide, mercaptan, ammonia, or aniline) and subsequently a ring closure and that the former is the primary process which controls the direction of the latter. The elimination may occur in two ways. If it can be conceived as occurring solely on one side of the molecule, and without closure of the ring, it yields compounds in which a cyanamide, carbimide, or thio-carbimide group is formed from a hydrazo-nitrogen atom. Since such strongly unsaturated hydrazides have never been isolated, it must be assumed that their tendency towards transformation is so marked that the equilibrium between them and the eliminated molecule on the one hand, and the original material on the other, remains strongly displaced in favour of the latter. It is, however, permanently disturbed when a group attached to a carbon atom at the other side of the molecule can

add itself at the unsaturated group whereby elimination is completed with closure of the ring. The second case is that in which the eliminated molecule can be produced only by simultaneous co-operation of groups attached at the ends of the molecule, so that elimination and ring closure are intimately associated. Elimination of mercaptan then occurs much less readily than in the first case, and is only possible under exceptionally favourable conditions, such as the acidity of the eliminated hydrogen atom.

In general, it is found that an acid medium favours the loss of ammonia or amine, whereas elimination of hydrogen sulphide or, particularly, of mercaptan occurs more readily in the presence of alkali. The groups, NH_2, NHR, SH, or SR, are most readily removed when attached to CO, with more difficulty when united to C(:NH)·SR, and with most difficulty from the group CS. Since the different factors overlap in the action, elimination frequently occurs in several directions, but each mode of loss in one and the same medium leads to only one ring closure.

The following substances are described. Potassium thiosemicarbazidedithiocarbonate, $NH_2·CS·NH·NH·CS_2K$, coarse, colourless crystals and the *di-silver* salt, $C_2H_3N_3S_3Ag_2$. *Methylthiosemicarbazidedithiocarbonate*, small, colourless crystals, m. p. 153°, and the corresponding dimethyl compound, $NH_2·CS·NH·N·C(SMe)_2$, small crystals, m. p. 106° (Busch and Biehler, A., 1916, i, 760, give m. p. 101—102°). *Methyl methylthiolsemicarbazidodithiocarbonate*, $NH_2·C(SMe):N·NH·CS_2Me$, from thiosemicarbazide-*S*-methyl ether and methyl chlorodithioformate, a crystalline powder, m. p. 133—135° when heated rapidly, and the corresponding trimethyl compound, $NH_2·C(SMe):N·N:C(SMe)_2$, m. p. 58—59° (Busch, *loc. cit.*, gives m. p. 60°). *Potassium semicarbazidedithiocarbonate*,

$$NH_2·CO·NH·NH·CS_2K.$$

Methyl semicarbazidedithiocarbonate, m. p. 193—194° (Busch, *loc. cit.*, gives m. p. 191—192°), which is converted by ferric chloride in acid solution into *thiourazole disulphide*, $C_3H_7ON_3S_2$, m. p. 246°, and by heating above its melting point into the *compound*, $\begin{matrix} N:C(SMe) \\ | \\ NH—CO \end{matrix}>S$, small prisms, m. p. 96°. *Dimethyl semicarbazidodithiocarbonate*, $NH_2·CO·NH·N:C(SMe)_2$, coarse leaflets, m. p. 124°. *Methyl methylthiolsemicarbazidothiocarbonate*,

$$NH_2·C(SMe):N·NH·CO·SMe,$$

m. p. 128° (decomp.), and the corresponding *trimethyl* compound, $NH_2·C(SMe):N·NMe·CO·SMe$, m. p. 185° (decomp.); the latter substance is transformed by sodium hydroxide solution into *N-methylthiourazole methyl ether*, small needles, m. p. 204°.

H. W.

The Yields of some Grignard Reagents. H. Gilman and R. McCracken (*J. Amer. Chem. Soc.*, 1923, 45, 2462—2466).—Using essentially the method of preparation (A., 1923, i, 193) which gives the best yield of magnesium ethyl iodide, and the method of analysis previously employed (A., 1923, ii, 272), the following yields are obtained of Grignard reagent from the halide mentioned.

n-Propyl iodide, 79·35, *n*-butyl iodide, 65·23, *n*-amyl iodide, 75·76, *n*-hexyl iodide, 59·50, *n*-heptyl iodide, 64·27, *n*-octyl iodide, 44·22, lauryl bromide, 73·70, *n*-butyl bromide, 91·23, *iso*butyl bromide, 78·23, *sec.*-butyl bromide, 68·26, *tert.*-butyl bromide, 20·62, *n*-butyl chloride, 87·38, bromobenzene, 94·37, iodobenzene, 84·58, *o*-bromotoluene, 86·65, *m*-bromotoluene, 84·75, *p*-bromotoluene, 88·16, benzyl chloride, 94·28, α-bromonaphthalene, 70·50, bromo*cyclo*hexane, 68·32, β-bromostyrene, 47·59% of theory. W. S. N.

Organo-zinc Compounds. A. Job and R. Reich (*Bull. Soc. chim.*, 1923, **33**, [iv], 1414—1433; cf. A., 1922, i, 645).—Details are given of the preparation of zinc ethyl iodide in ethereal solution and in ethyl acetate solution, also of methods of estimating organo-zinc and organo-magnesium compounds. Of the latter, the iodine method when modified by the elimination of various sources of error is stated to be the most accurate and satisfactory. Zinc ethyl iodide reacts with cuprous chloride, bromide, and cyanide yielding cuprous iodide and the corresponding zinc ethyl compound, ethyl acetate being the most suitable medium for the reaction. All three resulting substances with iodine yield ethyl iodide and zinc chloroiodide. Sodium acts on zinc ethyl iodide in ethereal solution with formation of sodium ethoxide, ethane, and ethylene, accompanied by liberation of metallic zinc. The equations given are $2ZnEtI+2Na \longrightarrow Zn+2NaI+ZnEt_2$; $ZnEt_2+2Na \longrightarrow 2NaEt+Zn$; $2NaEt+2Et_2O \longrightarrow 2OEtNa+2C_2H_4+2C_2H_6$. Finely divided calcium or magnesium have a similar action. Magnesium ethyl bromide reacts with zinc ethyl iodide with development of heat, but no products that would throw light on the nature of the reaction were isolated. Zinc compounds are stated to have considerable advantage over magnesium compounds for determining hydroxyl groups in organic substances and a detailed description of the method recommended is given together with the means of overcoming certain experimental difficulties. Unlike the corresponding magnesium compounds, the zinc alkyl iodides do not react with the oxygen atom of ketones or ethers, and thus, being without action on ketonic tautomerides, afford a means of observing and measuring the rate of transformation from the ketonic to the enolic form.

H. J. E.

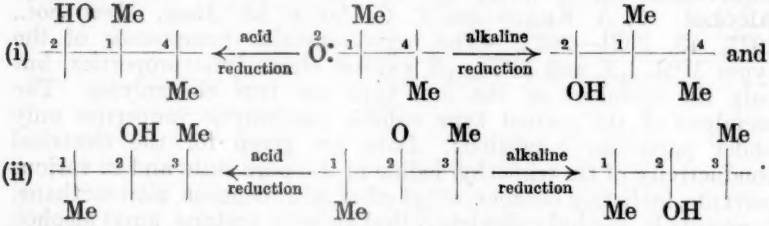
Propylstannonic Acid. J. G. F. Druce (*Chem. News*, 1923, **127**, 306—308).—α-*Propylstannonic acid* is obtained by shaking propyl bromide with an alkaline solution of potassium hydrogen stannite containing enough alcohol to give a homogeneous mixture, and, after fourteen days, neutralising with hydrochloric acid. It forms a gelatinous precipitate which dries to a white powder. The *potassium* salt, $C_3H_7SnO_2K$, is deliquescent. The acid also forms a *sodium* salt and basic *calcium* and *barium* salts. When distilled, the acid decomposes, giving a mixture of propane, propyl alcohol, water, and propylene, leaving a residue containing stannous and stannic oxides. When boiled with an excess of 10% potassium or sodium hydroxide, α-propylstannonic acid is converted into *tin dipropyl oxide*, $SnOPr^{\alpha}_2$, a white powder which decomposes

at high temperatures, leaving a residue of stannic oxide. *Tin propyl trichloride*, $SnPrCl_3$, is obtained by boiling α-propylstannonic acid with a benzene solution of hydrogen chloride; it forms colourless, deliquescent crystals. *Tin propyl tribromide* is obtained by dissolving α-propylstannonic acid in concentrated hydrobromic acid. E. H. R.

Organo-metallic Compounds. I. Introduction. II. Equivalent Conductivity of Tin Trimethyl Chloride in Ethyl Alcohol. C. A. KRAUS and C. C. CALLIS (*J. Amer. Chem. Soc.*, 1923, **45**, 2624—2632).—The organo-metallic compounds of the types $M^nR_{n+1}X$ and $M^nR_{n-1}X$ exhibit electrolytic properties, but only the members of the first type are true electrolytes. The members of the second type exhibit electrolytic properties only under particular conditions. Data are given for the electrical conductivity of tin trimethyl iodide in the pure state and in various solvents, including benzene, ethyl ether, nitrobenzene, nitromethane, benzonitrile, methyl salicylate, ethyl acetate, acetone, amyl alcohol, benzyl alcohol, pyridine, and ethyl alcohol. The pure compound is a poor conductor ($k=0{\cdot}3\times10^{-5}$), whilst solutions of this compound in solvents of the non-basic type are also poor conductors, even although the dielectric constant of the solvent may be high. Solutions in the alcohols and amines are relatively good conductors. The equivalent conductivity of tin trimethyl chloride in absolute alcohol at low concentrations ($0{\cdot}1566\times10^{-3}$—$16{\cdot}5707\times10^{-3}N$) has been measured at 25°. From these measurements, the value 30·8 is deduced for Λ_∞. Up to a concentration of $10^{-3}N$, the conductivity values conform to the law of mass action within the limits of experimental error. The mass action constant has the value $0{\cdot}349\times10^{-4}$. The properties of compounds of the type of tin trimethyl chloride are discussed. It is suggested that the electrolytic properties of solutions of this and similar compounds in the alcohols and amines are due to the formation of a more electropositive group by combination of the tin trimethyl group with the solvent. It is pointed out that the properties of tin trimethyl chloride correspond closely with the properties of methyl iodide and more particularly with those of the halogen acids. The properties of the tin trimethyl group and of its compounds may be accounted for on the basis of the electro-affinity of this group. The analogy which this group bears to hydrogen is pointed out. J. F. S.

The Stereochemistry of the Tri-substituted *cyclo*Hexanes. A. SKITA (*Ber.*, 1923, **56**, [*B*], 2234—2244; cf. Skita and Schenck, A., 1922, i, 240; Skita, A., 1923, i, 460, 671).—Although a considerable amount of information is available with regard to the formation of the theoretically possible, disubstituted *cyclo*hexanes, very little work has been done with trisubstituted compounds; the hydrogenation of *m*-4-xylidine and *m*-4-xylenol has, however, been studied to some extent. Reduction of the latter compound occurs in such a manner that the methyl groups occupy the trans-position relatively to one another. The present com-

munication adduces evidence to show that this behaviour is general since 1 : 4-dimethyl*cyclo*hexan-2-one and its oxime are reduced to mixtures of isomeric 1 : 4-dimethyl*cyclo*hexan-2-ols and 1 : 4-dimethyl*cyclo*hexyl-2-amines, whereas 1 : 3-dimethyl*cyclo*hexan-2-one and its oxime yield only a single 1 : 3-dimethyl*cyclo*hexan-2-ol and 1 : 3-dimethyl*cyclo*hexyl-2-amine, independently of the conditions under which reduction occurs. The results are explained in accordance with the schemes :



The fourth and sixth formulæ are identical.

[With L. WINTERHALDER and W. SCHNEIDER.]—*p*-2-Xylenol is converted by hydrogen in acid solution in the presence of colloidal platinum into a mixture of 1^c : 4^t-dimethyl*cyclo*hexane, b. p. 119·5°/atmospheric pressure, and 1^c : 4^t-*dimethyl*cyclo*hexan*-2^c-*ol*, a colourless liquid, b. p. 74°/14 mm., 180°/atmospheric pressure, d_4^{20} 0·9066, n_D^{20} 1·45377 (*phenylurethane*, needles, m. p. 113°). It is oxidised by Beckmann's chromic acid solution to 1^c : 4^t-*dimethyl*cyclo*hexan*-1-*one*, b. p. 178° (corr.); the *oxime*, needles, m. p. 111°, and the *semicarbazone*, leaflets, m. p. 173°, are described. Reduction of the ketone in an acid medium leads to the formation of 1^c : 4^t-dimethyl*cyclo*hexan-2^c-ol (see above), whereas it is transformed by treatment with sodium and moist ether into 1^t : 4^c-*dimethyl*cyclo*hexan*-2^c-*ol*, a liquid with a pleasant odour, b. p. 179° (corr.), d_4^{20} 0·9032, n_D^{20} 1·45297 (*phenylurethane*, crystals, m. p. 117°). Catalytic hydrogenation of 1^c : 4^t-dimethyl*cyclo*hexanoneoxime dissolved in acetic acid (50%) in the presence of colloidal platinum yields 1^c : 4^t-*dimethyl*cyclo*hexyl*-2^c-*amine*, b. p. 166° (corr.), d_4^{20} 0·8502, n_D^{20} 1·45247 (*benzoyl* derivative, m. p. 120°; *hydrochloride*, needles, m. p. 207°; *picrate*, golden-yellow leaflets, m. p. 175°; *phenylthiocarbamide* compound, long needles, m. p. 165°) whereas treatment of it with sodium and alcohol gives the isomeric 1^t : 4^c-*dimethyl*cyclo*hexyl*-2^c-*amine*, b. p. 164° (corr.), d_4^{20} 0·8420, n_D^{20} 1·44976 (*benzoyl* derivative, crystals, m. p. 175°; *hydrochloride*, small needles, m. p. 247°; *picrate*, yellow leaflets, m. p. 198°; *phenylthiocarbamide* derivative, m. p. 222°).

Hydrogenation of *p*-2-xylidine dissolved in a mixture of glacial acetic and concentrated hydrochloric acids in the presence of colloidal platinum yields a mixture of almost equal quantities of the stereoisomeric 2 : 5-dimethyl*cyclo*hexylamines described above, which are separated from one another by fractional crystallisation of the corresponding benzoyl derivatives; the mother-liquors contain relatively very small amounts of a third *benzoyl* derivative,

which is hydrolysed by concentrated hydrochloric acid to 1^c : 4^c-*dimethyl*cyclo*hexyl*-2^c-*amine*, b. p. 168° (corr.), d_4^{20} 0·8860.

Hydrogenation of *m*-2-xylenol dissolved in acetic and hydrochloric acids in the presence of colloidal platinum yields a mixture of 1^c : 3^t-dimethyl*cyclo*hexane, b. p. 118—119°, and 1^c : 3^t-*dimethyl*-cyclo*hexan*-2^c-*ol*, b. p. 172°, d_4^{20} 0·91618, n_D^{20} 1·46124 (*phenylurethane*, crystals, m. p. 158°). The alcohol is oxidised by Beckmann's chromic acid mixture to 1^c : 3^t-*dimethyl*cyclo*hexanone*, b. p. 174° (*oxime*, crystals, m. p. 86°; *semicarbazone*, m. p. 198°). The ketone is converted by catalytic hydrogenation in acid solution or by means of sodium and moist ether into 1^c : 3^t-dimethyl*cyclo*-hexan-2^c-ol, which is identical with the product described above. Reduction of the oxime of the ketone, whether in acid or alkaline solution, yields 1^c : 3^t-*dimethyl*cyclo*hexyl*-2^c-*amine*, b. p. 73°/29 mm., 167°/atmospheric pressure, d_4^{20} 0·8564, n_D^{20} 1·4549 (*benzoyl* derivative, m. p. 197°; *hydrochloride*, colourless crystals, decomp. 282°; *picrate*, yellow crystals, m. p. 191°; *acetyl* compound, m. p. 198°; *phenyl-carbamide* derivative, m. p. 205°; *phenylthiocarbamide* compound).

Catalytic reduction of *m*-2-xylidine in acid solution in the presence of colloidal platinum gives mainly (90%) 1^c : 3^t-dimethyl*cyclo*-hexyl-2^c-amine; the crude product of the reaction is benzoylated, and the benzoyl derivatives are fractionally crystallised from glacial acetic acid, whereby in addition to the compound, m. p. 195°, a second *benzoyl* derivative, m. p. 121°, is isolated. The latter compound is hydrolysed to 1^c : 3^c-*dimethyl*cyclo*hexyl*-2^c-*amine*, b. p. 168·5, d_4^{20} 0·8625 (*hydrochloride*, m. p. 266° after softening at 263°). H. W.

Identification of Amines. C. S. Marvel and F. E. Smith (*J. Amer. Chem. Soc.*, 1923, **45**, 2696—2698).—p-*Bromobenzene-sulphonalkylamides*, having the m. p. stated, have been prepared from the following amines. Methylamine, m. p. 77°; benzylamine, m. p. 117°; dimethylamine, m. p. 94°; piperidine, m. p. 91°; *o*-toluidine, m. p. 116°; *p*-toluidine, m. p. 98°; *o*-chloroaniline, m. p. 105°; *p*-chloroaniline, m. p. 134°; *p*-bromoaniline, m. p. 145°; *p*-anisidine, m. p. 142°; *p*-phenetidine, m. p. 143°; α-naphthylamine, m. p. 183·5°; β-naphthylamine, m. p. 129°; methylaniline, m. p. 92°; ethylaniline, m. p. 91°; propylaniline, m. p. 109°; butylaniline, m. p. 87°; *p*-bromoethylaniline, m. p. 118·5°. p-*Bromoethylaniline*, b. p. 143—147°/20 mm., is prepared by brominating ethylaniline in glacial acetic acid solution.

W. S. N.

Aromatic Sulphonic Acids and Sulphones. H. Meyer [with, in part, W. Schmidt and R. Grim] (*Annalen*, 1923, **433**, 327—350).—In the preparation of sulphonic acids, it is practicable, and more economical, to use an excess of hydrocarbon, rather than of sulphuric acid; when the mixture is boiled, the water formed in the reaction distils off in the hydrocarbon vapour. In the sulphonation of a non-volatile hydrocarbon, carbon tetrachloride is added. An apparatus is described in which the hydrocarbon or solvent vapour is condensed, and the liquid dried and returned

to the reaction flask; the water formed is run off periodically from the drying apparatus, the quantity collected recording on the progress of the reaction. The conversion of the sulphuric acid, which, moreover, need not be highly concentrated, is practically quantitative; also, an anhydrous product is isolated, merely by distilling off the excess of hydrocarbon. The following sulphonic acids have been prepared by this method. Benzenesulphonic acid, $+H_2O$; toluenesulphonic acid, $+H_2O$; *p*-xylenesulphonic acid, $+2H_2O$; chlorobenzenesulphonic acid, $+H_2O$; naphthalenesulphonic acid (85·3% β-acid and 14·7% α-acid), and anisolesulphonic acid. Naphthalene or anisole is sulphonated in the presence of carbon tetrachloride. In the sulphonation of toluene, vanadic acid or mercuric sulphate, but not kieselguhr or animal charcoal, acts as a catalyst.

In preparing anhydrides of sulphonic acids (Meyer and Schlegl, A., 1913, i, 608) it is advisable, but not always necessary, to use the pure alkali salt of the acid, and pure thionyl chloride. Toluene-*p*-sulphonic anhydride has now been obtained pure in this way; it forms colourless crystals, m. p. 125°. m-*Xylenesulphonic anhydride*, m. p. 139°, is somewhat readily decomposed by contact with moist air. When *m*-xylenesulphonic acid and thionyl chloride are heated at 160° for three to four hours, the products are 4-chloro-*m*-xylene, b. p. 186°; 4 : 6-dichloro-*m*-xylene, m. p. 68°, b. p. 220—230°; and a crystalline compound, m. p. 112°, perhaps identical with the trichloro-*m*-xylene of Claus and Burstert (A., 1890, 1105).

During the formation of sulphonic acids, traces of sulphones are generally produced; the yield of sulphone is greater if the reaction is continued at a higher temperature (sealed tube), or if the hydrocarbon employed has a high b. p. (*e.g.*, anisole). Simple or mixed sulphones may be conveniently prepared by passing the vapour of a hydrocarbon over a sulphonic acid, heated at, say, 150°; the issuing vapour is condensed, the water removed, and the dried liquid returned to be used again. Di-*p*-tolylsulphone is oxidised by means of 3% potassium permanganate solution to dicarboxydiphenylsulphone, m. p. 370° (cf. Michael and Adair, A., 1878, 415); *dimethyl* ester, slender, white needles, m. p. 194°; *diethyl* ester, glistening scales, m. p. 158°; *dichloride*, needles, *diamide*, glistening scales, m. p. 384°; *dianilide*, small, faintly rose-coloured leaflets, m. p. 376°. The diamide is converted by Hofmann's method into di-*p*-aminophenylsulphone. The action of concentrated nitric acid on a cold solution of ditolylsulphone in concentrated sulphuric acid gives 3 : 3′-*dinitroditolylsulphone*, pale yellow plates, m. p. 160°; 3 : 5 : 3′ : 5′-*tetranitroditolylsulphone*, colourless needles, m. p. 266°, is formed at 100°. The reduction of the dinitro-compound by means of boiling glacial acetic acid, concentrated hydrochloric acid, and zinc powder, gives 3 : 3′-*diaminoditolylsulphone*, glistening, faintly rose-coloured leaflets, m. p. 154°; *diacetyl* derivative, colourless leaflets, m. p. 197°. *Di*-m-*xylylsulphone*, elongated, rhombic prisms, m. p. 121°, is oxidised by means of permanganate to a *tetracarboxylic acid*, monoclinic tablets, m. p. 294° (decomp.); *tetraethyl* ester, microscopic tablets,

m. p. 235° (decomp.). *Dimesitylsulphone* forms slender, colourless needles, m. p. 195°. *Ditetrahydronaphthylsulphone* forms colourless needles, m. p. 135°; it is obtained by the action of the hydrocarbon vapour on concentrated sulphuric acid at 220°, or by the condensation of the hydrocarbon with the sulphonyl chloride in the presence of aluminium chloride. Phenyltolylsulphone is prepared from toluene and benzenesulphonic acid, or from benzene and toluenesulphonic acid, at 135—140°; it is gradually decomposed by the action of chlorine at 130°, giving benzenesulphonyl chloride, and a *chlorophenyltolylsulphone*, long needles, m. p. 126°. p-*Tolyl*-m-*xylylsulphone*, aggregates of long, slender prisms, m. p. 121°, is prepared from toluene and *m*-xylenesulphonic acid at 170—180°, or from *m*-xylene, toluene-*p*-sulphonyl chloride, and aluminium trichloride. *Phenyl-ψ-cumylsulphone*, m. p. 160°, from benzene and ψ-cumenesulphonic acid at 150°. p-*Tolyl-ψ-cumylsulphone*, m. p. 159°. m-*Xylyl-ψ-cumylsulphone*, m. p. 125°. *Phenylmesitylsulphone*, glistening leaflets, m. p. 116°. *Tolylmesitylsulphone*, needles, m. p. 119°, from mesitylene and toluenesulphonyl chloride, or from toluene and mesitylenesulphonyl chloride, in the presence of aluminium chloride. m-*Xylylmesitylsulphone*, long, rectangular plates, m. p. 149°. Phenyl-*p*-chlorophenylsulphone, m. p. 91°. p-*Chlorophenyl*-p-*tolylsulphone*, rhombic leaflets, m. p. 128°, is converted by the action of chlorine into *p*-chlorobenzoyl chloride and a *dichlorophenyltolylsulphone*, clusters of needles, m. p. 120—121°. *Tolyl*-β-*naphthylsulphone*, small leaflets, m. p. 154°. m-*Xylyl*-β-*naphthylsulphone*, colourless leaflets, m. p. 128°. p-*Chlorophenyl*-β-*naphthylsulphone*, m. p. about 136°. *Tolyltetrahydronaphthylsulphone*, m. p. 112°. *Phenyltetrahydronaphthylsulphone*, needles, m. p. 78°. m-*Xylyltetrahydronaphthylsulphone*, rhombs, m. p. 78°. p-*Xylyltetrahydronaphthylsulphone*, rhombic leaflets, m. p. 115°. *Mesityltetrahydronaphthylsulphone*, slender needles, m. p. 105°. p-*Chlorophenyltetrahydronaphthylsulphone*, colourless needles, m. p. 136°. The action of toluene vapour at 130° on α-naphthalenesulphonic acid gives naphthalene, toluenesulphonic acid, and ditolylsulphone; benzene has a similar action. *Tolyl*-α-*naphthylsulphone*, hard, glistening leaflets, m. p. 122°, and m-*xylyl*-α-*naphthylsulphone*, small, white leaflets, m. p. 119°, can, however, be obtained with the aid of aluminium chloride. Since *p*-dichlorobenzenesulphonic acid behaves like α-naphthalenesulphonic acid, p-*dichlorophenyl*-p-*tolylsulphone*, leaflets, m. p. 139°, and p-*dichlorophenyl*-m-*xylylsulphone*, slender, colourless needles, m. p. 135°, are also prepared by the aluminium chloride method. *o*-Chlorotoluene-*p*-sulphonic acid decomposes above 110°, with elimination of hydrogen chloride, and formation of toluenesulphonic acid; consequently, by the action of *m*-xylene vapour or toluene vapour, tolylxylylsulphone or ditolylsulphone, respectively, is produced.

[With L. Steinmetzer.]—When toluene vapour is allowed to act on phenol-*p*-sulphonic acid at 150—160°, the latter decomposes into *di*-p-*hydroxydiphenylsulphone*, clusters of large needles, m. p. 239° (*dibenzoate*, m. p. 243°), and sulphuric acid; consequently, di-*p*-tolylsulphone also appears in the product, together with

resinous material. With benzene or *m*-xylene, the second sulphone is not formed, owing to excessive resinification. Phenol-*o*-sulphonic acid behaves like the para-derivative, but the action of toluene or xylene at 150° on phenol-2 : 4-disulphonic acid gives di-*p*-tolyl-sulphone or dixylylsulphone; thus the elimination of the first sulphonic acid radicle proceeds much more rapidly than that of the second. *p*-Cresolsulphonic acid is evidently more stable, since it reacts normally with benzene vapour at 140° or with toluene vapour at 150°, to give, respectively, *phenyl*-p-*cresolsulphone*, microscopic leaflets, m. p. 195° (decomp.) (violet coloration with ferric chloride), or *tolyl*-p-*cresolsulphone*, quadratic leaflets, m. p. 58°. 2-*Tetrahydronaphthol*-3-*phenylsulphone*, white leaflets, m. p. 197°, is obtained from benzene vapour and tetrahydronaphthol-sulphonic acid at 110—120°. The methyl ether of this acid, $+2H_2O$, has m. p. 165°, and not 107°, as generally stated; it cannot be converted into a sulphone.

Methyl*cyclo*hexane cannot be used as a solvent in place of carbon tetrachloride, since even at 100° it is dehydrogenated by the action of 96% sulphuric acid, and converted into toluene-*p*-sulphonic acid.

W. S. N.

The Constitution of the *m*-Xylenedisulphonyl Chlorides. J. POLLAK and O. LUSTIG (*Annalen*, 1923, **433**, 191—201).—Doubt has already been thrown (Pollak and Schadler, A., 1918, i, 497; Pollak and Rudich, A., 1923, i, 27) on the constitutions assigned by Pfannenstill (A., 1892, 1340) to the *m*-xylenedisulphonyl chlorides. The solid isomeride, m. p. 130° (cf. Wischin, A., 1891, 73; also Pfannenstill, *loc. cit.*), is now shown to be *m*-xylene-4 : 6-disulphonyl chloride; the oily dichloride is, perhaps, *m*-xylene-2 : 4-disulphonyl chloride, but further experimental work is required, and is in progress.

The chloride, m. p. 130°, is synthesised by a method which leaves no doubt as to its structure. *m*-Xylene-4-sulphonic acid must have the formula assigned to it, since it gives, on nitration, three isomeric mono-nitro-derivatives, one of which is also obtained by sulphonating 4-nitro-*m*-xylene, and must therefore be 6-nitro-*m*-xylene-4-sulphonic acid (Claus and Schmidt, A., 1886, 708). 6-Nitro-*m*-xylene-4-sulphonic acid, the purity of which is shown by conversion into its chloride, m. p. 98°, is reduced by means of ammonium sulphide to the 6-amino-derivative, which is diazotised, and then treated in neutral solution with potassium xanthate. The product is hydrolysed by means of alkali hydroxide, and oxidised by means of potassium permanganate. The resulting acid is treated with phosphorus pentachloride, with the production of *m*-xylene-4 : 6-disulphonyl chloride, identical with the chloride obtained by Wischin (*loc. cit.*) and by Pfannenstill (*loc. cit.*). Incidentally, the same compound may more conveniently be prepared by heating *m*-xylene or *m*-xylene-4-sulphonic acid (or its sodium salt) with seven times its weight of chlorosulphonic acid at 150—160°.

Pfannenstill's formulæ were based on the production of the solid chloride, not only from *m*-xylene-4-sulphonic acid, but also,

together with an oily isomeride, from the 2-sulphonic acid. Apparently the latter must have been impure; but a more likely explanation is that, during further sulphonation, isomerisation to the 4-sulphonic acid first occurs, this being actually known to occur during the sulphonation of benzene (Behrend and Mertelsmann, A., 1911, i, 189).

The action of cold nitric acid, *d* 1·52, on *m*-xylene-4-sulphonic acid gives 2 : 6-dinitro-*m*-xylene-4-sulphonic acid, which is identified by conversion into its chloride (Limpricht and Gronow, A., 1885, 1232).

The action of chlorosulphonic acid, seven parts, on *p*-xylene at 150—160° gives isomeric disulphonyl chlorides, (*a*) large crystals, m. p. 81°, (*b*) small crystals, m. p. 164°, in the ratio 10 : 1 (cf. Pfannenstill, *loc. cit.*; also Holmes, A., 1891, 1374), the former of which is provisionally designated *p*-xylene-2 : 6-disulphonyl chloride.

W. S. N.

Stereoisomerism among Derivatives of Diphenyl. T. M. Lowry (*Nature*, 1923, **112**, 654).—In the use of Dewar's formula for benzene (*e.g.*, Turner, A., 1923, i, 1085; Kenner, *ibid.*), the para-linking should be regarded as indicating only the existence of "free affinities" on the 1 and 4 carbon atoms, or of an electrovalency between them. The length of the carbon-to-carbon bond is constant at about 1·5 Å., but there is no justification for assuming consequent distortion of the hexagon to the quadrilateral

A. A. E.

Preparation of Hydrogenation Products of Naphthalene and its Derivatives. Chemische Fabrik Griesheim-Elektron (D.R.-P. 370974; from *Chem. Zentr.*, 1923, [iv], 539).—Water is allowed to act slowly on a mixture of alkali metals with a solution of naphthalene or its derivatives in an indifferent solvent. For example, by slow addition of water to a mixture of naphthalene and metallic sodium in solvent naphtha at 145°, tetrahydronaphthalene is obtained. When a mixture of aliphatic hydrocarbons of b. p. 115—120° is used in place of solvent naphtha, dihydronaphthalene is obtained. α-Naphthylamine is similarly hydrogenated to tetrahydro-α-naphthylamine, and β-naphthol ethyl ether to *tetrahydro-β-naphthyl ethyl ether*, an oil, b. p. 155°/28 mm., having a pleasant odour. It is identical with the product obtained by ethylation of *tetrahydro-β-naphthol*.

G. W. R.

Stereoisomerism of Decahydronaphthalene and its Derivatives. W. Hückel (*Nach. K. Ges. Wiss. Göttingen*, 1923, 43—56; from *Chem. Zentr.*, 1923, iii, 766—767).—The author's investigations on decahydro-β-naphthol (decalol) render the existence of cis- and trans-isomerides of decahydronaphthalene probable. The assumption of Mascarelli (A., 1911, i, 964—965) that the two components of decahydro-β-naphthol of m. p. 75° and 105°, respectively, have the hydroxyls in *cis*- and *trans*-positions is held to be erroneous, since the author has obtained different products on

oxidising them. By oxidation of the decalol of m. p. 105°, a decalone is obtained having d_4^{20} 1·005, whilst from the decalol having m. p. 75° a decalone having d_4^{20} 0·975 is obtained. Both give the corresponding decalols on reduction. By the further oxidation of both ketones, there is the possibility of the formation of two acids of the composition $C_{10}H_{16}O_4$, namely, *cyclo*hexane-1 : 2-diacetic acid, $C_6H_{10}(CH_2{\cdot}CO_2H)_2$ (I) and 2-carboxy*cyclo*hexane-1-propionic acid, $CO_2H{\cdot}C_6H_{10}{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$ (II). From the one ketone the *cis*- and from the other ketone the *trans*-form of one or both of these acids should be obtainable. Both forms of I are unknown, but the *cis*- and *trans*-forms of II have been obtained (Windaus and Hückel, A., 1922, i, 658). The decalol of m. p. 105° gives on oxidation with alkaline potassium permanganate a mixture of two acids of m. p. 101° and 159—161°, respectively, whilst the decalol of m. p. 75°, similarly oxidised, gives acids of m. p. 143° and 167°, respectively. The acids of m. p. 101° and 143° were identical with the *cis*- and *trans*-forms of II, so that the other acids must be the *cis*- and *trans*-forms of I. The contradictory data obtained for the melting points and densities of decahydronaphthalene are due to the occurrence of mixtures of *cis*- and *trans*-forms. *Cis*-β-Decahydronaphthol, m. p. 105°, prepared by hydrogenation of *ac*-β-tetrahydronaphthol, gives cis-β-*decahydronaphthalone*, b. p. 247°/755 mm.; d_4^{21} 1·0039; n_D^{21} 1·49180; the *semicarbazone* has m. p. 182—183°; the *oxime* is a viscid oil. Hydrogenation of *o*-carboxyphenylpropionic acid gives *cis*-2-carboxy*cyclo*hexane-1-propionic acid, m. p. 109—110°. The *diethyl* ester has b. p. 315—320°/760 mm. and 183°/20 mm.; the *dianilide* has m. p. 200° immediately after preparation; after keeping for one month, the m. p. is 163°. *trans*-β-Decahydronaphthalone gives a *semicarbazone* with m. p. 192—193°; the *oxime* has m. p. 75°. trans-*Decahydronaphthalene* has b. p. 185°/753 mm.; d_4^{20} 0·872; n_D^{20} 1·47009. cis-*Decahydronaphthalene* has b. p. 193°; d_4^{20} 0·898; n_D^{20} 1·48279. G. W. R.

Chlorination of Decalin [Decahydronaphthalene]. I. W. Borsche and E. Lange (*Annalen*, 1923, **434**, 219—236).—Hückel (preceding abstract) has shown that decalin is a mixture of *cis*- and *trans*-forms, a fact unknown to Leroux (A., 1904, i, 986), some difficulties connected with the results of the latter author now being removed.

Chlorination of decalin, corresponding with the introduction of one chlorine atom, affords only 25% of 2-chlorodecahydronaphthalene (b. p. 121—122°/18 mm.) (see below). The latter is, further, a mixture of *cis*- and *trans*-forms. cis-β-*Chlorodecahydronapththalene* from the decahydronaphthol of m. p. 102—104°, has b. p. 110—112°/15 mm. The *trans*-isomeride (from the decahydronaphthol of m. p. 76°) has not been obtained pure. The mixture of chlorodecalins, on heating with aniline, affords a mixture (b. p. 76—80°/15 mm.) of Δ^1- and Δ^2-octahydronaphthalenes (octalins), the former in larger quantity; this is proved by the results of oxidation, when (besides oxalic acid, and an *acid*, $C_{10}H_{16}O_5$ or $C_{10}H_{18}O_5$,

leaflets, m. p. 116—118° [indef.]), *o*-carboxy*cyclo*hexanepropionic acid, and a smaller quantity of *cyclo*hexane-1 : 2-diacetic acid (mixture of *cis*- and *trans*-forms, m. p. 152—153°) are formed.

The calcium salt of *o*-carboxy*cyclo*hexanepropionic acid, on heating, gives the hexahydro-α-hydrindone described by Windaus, Hückel, and Reverey (A., 1923, i, 220).

The above mixture of *cis*- and *trans-cyclo*hexane-1 : 2-diacetic acids cannot be separated by distilling (b. p. 170—180°/10 mm.) or by repeated fractional crystallisation; nor can an artificial mixture (m. p. 152—153°) of the individual acids be separated (the cis-*acid*, m. p. 158—160°, being obtained by oxidising *cis*-2-octahydronaphthalene; the *trans*-acid [Leroux] having m. p. 167°). Similarly, on conversion into derivatives, mixtures of *cis*- and *trans*-forms of these acids are obtained, with the following constants: *diamide*, m. p. 274—275°; *dianilide*, m. p. 295—300° (decomp.); *anhydride*, resin, b. p. 180°/10 mm.; *ethyl* ester, b. p. 147°/7 mm. Again, *hexahydro-2-hydrindone*, obtained from the mixture of acids by (1) distilling with acetic anhydride, (2) heating with concentrated hydrochloric acid at 180—200°, (3) heating the calcium salts, or (4) the action of sodium on the ester (followed by hydrolysis, etc.), is a mixture. The latter gives a 2-*nitro*-4-*cyano*-*phenylhydrazone*, orange-red needles, m. p. 190—192°, and a *semi-carbazone*, white leaflets, m. p. (decomp.) 235° or 240° (with slow or rapid heating, respectively), regenerating the mixture of hydrindones (b. p. 108—112°/15 mm.) when treated with oxalic acid.

Since the *cyclo*hexanediacetic acid (m. p. 167°) obtained by Leroux is now shown to be the *trans*-form, his 2 : 3-decahydronaphthalene glycols and his dibromodecahydronaphthalene (m. p. 85°) must also have been derivatives of *trans*-decalin.

A Grignard reagent prepared from the above mixture of 2-chlorodecalins, on treating with carbon dioxide, etc., gives a mixture of the cis- and trans-*decahydronaphthalene-2-carboxylic acids*, which may be separated through the *amides* (m. p. 165—166° and 195°, respectively). The *cis*-acid is a resin, b. p. 150°/15 mm. (*anilide*, needles, m. p. 128—130°), the *trans*-acid having m. p. 103° (*anilide*, needles, m. p. 155—158°).

The above mixture of octahydronaphthalenes, gives, as isolable products, a dibromide, m. p. 170°, together with some hexahydronaphthalenetetrabromide (m. p. 184°), owing to the presence of dichlorodecahydronaphthalenes in the original chlorodecalin mixture.

Pure cis-2-*octahydronaphthalene* (b. p. 72—73°/15 mm.; from *cis*-2-chlorodecalin) gives a *dibromide*, m. p. 170°, which, however, cannot be converted into the corresponding dihydroxy-compound and so oxidised to acids of known configuration.

The original decalin chlorination mixture contains dichlorodecahydronaphthalenes (b. p. 148—150°/18 mm.), converted by aniline into hexahydronaphthalenes (b. p. 75—85°/15 mm.). The latter, with bromine, give a mixture of *hexahydronaphthalenetetrabromides* (m. p. 184° and 200°, respectively) and 2-octahydronaphthalene-dibromide (m. p. 170°) and, on oxidation with permanganate affords

a mixture of oxalic acid, *cyclo*hexane-1 : 2-diacetic acid, and a *hexahydrophthalic* acid (*methyl* ester, b. p. 175—180°/15 mm.).
E. E. T.

***m*-Chloroaniline and *m*-Chlorophenol.** I. J. RINKES (*Rec. trav. chim.*, 1923, **42**, 1092).—Seekles (A., 1923, i, 237) has overlooked data published by Holleman and Rinkes (A., 1911, i, 535). The m. p. of *m*-chloroaniline has been re-determined by Blanksma, and the figure −10·4° confirmed. E. E. T.

The Catalytic Reduction of the Multiple Carbon–Nitrogen Linking. K. W. ROSENMUND and E. PFANKUCH (*Ber.*, 1923, **56**, [*B*], 2258—2262).—An account of partly completed work induced by the recent publications of Taipale (A., 1923, i, 547, 905; Lochte and Bailey, A., 1922, i, 329; 1923, i, 26, 906).

It is shown that the catalytic reduction of oxime acetates may proceed in a manner differing from that of the oximes themselves, since gallaldoxime gives digallylamine, whereas its acetate yields gallylamine. Similarly, benzaldoxime acetate and benzophenoneoxime acetate give better yields of the corresponding primary amines than those obtained from the oximes.

The catalytic reduction of nitriles in glacial acetic acid solution in the presence of palladium leads to the production of primary amines, whereas Paal and Gerum (A., 1909, i, 381) and Rupe and Glenz (A., 1923, i, 100) have obtained mainly secondary amines by working in the presence of aqueous alcohol or a neutral solvent. The reaction is facilitated by the addition of hydrogen chloride or concentrated sulphuric acid. Phenylacetonitrile yields β-phenylethylamine; *o*-chlorobenzonitrile gives *o*-chlorobenzylamine in the presence of concentrated sulphuric acid, and benzylamine in the presence of sodium acetate. *p*-Hydroxyphenylacetonitrile, on the other hand, forms di-β-*p*-hydroxyphenylethylamine, which does not appear to be accompanied by the primary base. The production of the secondary base is attributed to the elimination of ammonia from the primary amine in the immediate vicinity of the catalyst, and thus resembles the catalytic formation of ethers during the reduction of aldehydes. The change can be inhibited to some extent by the addition of quinoline, which causes the production of appreciable quantities of β-*p*-hydroxyphenylethylamine in addition to the secondary base.

Helianthin is smoothly reduced to *p*-aminodimethylaniline and sulphanilic acid. Somewhat unexpectedly, particularly when considered in the light of Taipale's experiences with aliphatic azines (*loc. cit.*), it is found that benzylideneazine and *o*-hydroxybenzylideneazine yield the corresponding primary amines. Benzylideneaniline and benzophenoneanil yield aniline and (?) toluene or diphenylmethane, respectively. The formation of intermediate products such as benzylaniline appears to be excluded, since they are not further reducible.

The following observations are incidentally recorded. Benzophenoneoxime acetate has m. p. 69—70° instead of 55° as recorded in the literature. *Benzhydrylamine hydrochloride*, $C_{13}H_{14}NCl$, has

m. p. 270°. *Di*-β-p-*hydroxyphenylethylamine* crystallises in hexagonal platelets, m. p. about 190° (*hydrochloride*, m. p. 221—223°). H. W.

Preparation of Highly Chlorinated Hydroaromatic Products containing Nitrogen. Société Anonyme ancien. Durand, Huguenin et Cie (Brit. Pat. 193843).—The hydrochlorides of aromatic amines are chlorinated with gaseous chlorine in dry inert solvents, such as benzene or chlorobenzene to yield highly chlorinated hydroaromatic compounds containing nitrogen. Aniline dissolved in chlorobenzene, on saturation with hydrogen chloride and treatment with chlorine at 100° for two hours yields 1-*chloroimino*-2 : 2 : 3 : 4 : 4 : 5 : 6 : 6-*octachloro*cyclo*hexane*, m. p. 151°. If benzene is used as solvent and chlorine led in at a lower temperature and its introduction stopped as soon as dissolution is complete, 4-*chloroimino*-1 : 3 : 3 : 5 : 5 : 6-*hexachloro*cyclo*hexene* or 3-*chloroimino*-2 : 4 : 4 : 5 : 6 : 6-*hexachloro*cyclo*hexene* (the constitution doubtful), m. p. 125°, is produced. Both these substances are stable, decomposition first occurring at 170°. α-Naphthylaminehydrochloride suspended in chlorobenzene and treated with chlorine at 100° yields 1-*chloroimino*-2 : 2 : 3 : 4 : 4-*pentachlorotetrahydronaphthalene*, m. p. 122°; β-naphthylamine hydrochloride reacts even more readily, and treated in benzene at the ordinary temperature gives 2-*chloroimino*-1 : 1 : 3 : 3 : 4-*pentachlorotetrahydronaphthalene*, m. p. 118·5°. The aminoanthraquinones behave similarly to the naphthylamines; from the α-compound, 1-*chloroimino*-2 : 2 : 3 : 4 : 4-*pentachlorotetrahydroanthraquinone*, m. p. 190°, and from the β-compound, 2-*chloroketimino*-1 : 1 : 3 : 3 : 4-*pentachlorotetrahydroanthraquinone*, m. p. 210°, are produced. T. S. W.

The Action of Hypobromous Acid on Phenol and some Phenol Derivatives. E. Biilmann and E. Rimbert (*Bull. Soc. chim.*, 1923, **33**, [iv], 1473—1481).—2 : 4 : 6-Tribromophenol, 2 : 4 : 6-tribromo-*m*-cresol, 2 : 6-dibromo-*p*-nitrophenol, 4 : 6-dibromo-*o*-nitrophenol, 3 : 5-dibromosalicylic acid, and 3-bromoanisic acid were obtained by the action of hypobromous acid on the corresponding phenols, nitrophenols, and acids. Hypobromous acid reacts with β-methoxymethylmelilotic acid (cf. Biilmann and Starcke, A., 1912, i, 461), yielding 5-*bromo*-2-*methoxymethylmelilotic acid*,

$$OMe\cdot C_6H_3Br\cdot CH(OMe)\cdot CH_2\cdot CO_2H,$$

white needles, m. p. 126·5—127°, which on treatment with hydrochloric acid is converted into 5-*bromomethylcoumaric acid*,

$$OMe\cdot C_6H_3Br\cdot CH{:}CH\cdot CO_2H,$$

white needles, m. p. 222—223°. The latter, on treatment with permanganate, is oxidised to 5-bromo-2-methoxybenzoic acid, whilst the action of a solution of bromine in carbon disulphide results in the formation of αβ-5-tribromomethylmelilotic acid. This has m. p. 201°, not 197° as stated by Biilmann and Lund (A., 1923, i, 219). β-Methoxymethylmelilotic acid on treatment with hydrochloric acid yields methylcoumaric acid, which is also obtained from the same reagent and the mercuric compound of methoxymethylmelilotic acid. H. J. E.

The Kinetic Behaviour of Mixtures of Isomeric Nitrophenols in the Reduction with Stannous Chloride. A. KLEMENC [with A. KLEIN] (*Annalen*, 1923, **433**, 351—357).—The velocity constants (bimolecular) for the reduction by means of hydrochloric acid and stannous chloride of *o*-nitrophenol, *m*-nitrophenol, and *p*-nitrophenol have been measured, and Goldschmidt and Sunde's figures (A., 1906, i, 734) for the ortho- and meta-compounds and their calculated value for the para-derivative are confirmed. Measurements have also been made of the velocity of reduction of mixtures of *o*- and *p*-nitrophenols, and of *m*- and *p*-nitrophenols. The mixture behaves as though only one compound were present, in a concentration equal to the total concentration of the two isomerides, a bimolecular velocity constant being thus attained; in other words, the reduction of each individual does not proceed independently, as was found by van't Hoff ("Études," 1884, 96) for the isomeric dibromosuccinic acids. It follows that the relative concentrations of isomeric nitrophenols cannot be determined in this way, although this might be possible by the use of a different reducing agent. W. S. N.

The Influence of Substitution in the Components of Binary Solution Equilibria. XLII. The Binary Systems of Succinimide with Phenols. R. KREMANN and K. DIETRICH (*Monatsh.*, 1923, **44**, 151—162).—The freezing-point curves of mixtures of various phenols with succinimide have been plotted. With phenol, the curve indicates a compound between equal molecular proportions. A similar compound is formed with β-naphthol, but in agreement with the generally smaller tendency of α-naphthol to form additive compounds, the curve for the latter is a simple eutectic, with no indication at all of combination. With pyrogallol and the three dihydroxybenzenes, simple molecular compounds are formed in each case in the molecular proportion 1 : 1. The introduction of nitro-groups diminishes the tendency to form additive compounds; *p*-nitrophenol, in which the nitro-group is farthest away from the hydroxyl group, forms an additive compound (1 : 1), but no compounds are formed with *o*- or *m*-nitrophenol, or with 2 : 4-dinitrophenol or picric acid. S. I. L.

The Temperature of Explosion for Endothermic Substances. II. Trinitro-*m*-cresolates and their Explosion Temperatures. R. L. DATTA, L. MISRA, and J. C. BARDHAN (*J. Amer. Chem. Soc.*, 1923, **45**, 2430—2433; cf. Datta and Chatterjee, T., 1919, **115**, 1006).—The temperature of explosion may be determined by the method previously used with an accuracy, apparently, of 1°; it is quite characteristic, and, if a melting- or boiling-point cannot be taken, should be of value in characterising, or ascertaining the purity of, endothermic substances.

A series of additive compounds of trinitro-*m*-cresol has been examined. In the following, "T" stands for $OH{\cdot}C_6HMe(NO_2)_3$, and "E.p." for the explosion temperature; the names of the second constituent of the trinitrocresolates are given, the formula of the additive complex, and its properties. *Acenaphthene*, $C_{12}H_{10}$,2T,

yellow feathers, m. p. 120°, E.p. 451°; *fluorene*, $C_{13}H_{10}$,T, deep yellow needles, m. p. 109°, E.p. 421°; *allylamine*, $3C_3H_7N$,T, lustrous yellow (? crystals), m. p. 165°, E.p. 265°; *benzylamine*, C_7H_9N,T, golden-yellow needles, m. p. 185°, E.p. 406°; *camphylamine*, $C_{10}H_{19}N$,2T, lemon-yellow needles, m. p. 183°, E.p. 391°; *menthylamine*, $C_{10}H_{21}N$,2T, lemon-yellow needles, m. p. 200° (decomp.), E.p. 410°; *piperazine*, $2C_4H_{10}N_2$,T, lemon-yellow needles, m. p. 220—225° (decomp.), E.p. 359°; *α-naphthylamine*, $C_{10}H_9N$,T, dirty-yellow needles, m. p. 165—170° (decomp.), E.p. 470°; *p-chloroaniline*, C_6H_6NCl,2T, lemon-yellow needles, m. p. 170—172°, E.p. 449°; *p-bromoaniline*, C_6H_6NBr,2T, lemon-yellow granules, m. p. 172·5°, E.p. 441°; *p-iodoaniline*, C_6H_6NI,2T, bright yellow needles, m. p. 152°, E.p. 466°; *o-anisidine*, $OMe\cdot C_6H_4\cdot NH_2$,T, pale-yellow needles, m. p. 178° (decomp.), E.p. 349°; *o-phenetidine*, $OEt\cdot C_6H_4\cdot NH_2$,T, bright yellow needles, m. p. 165°, E.p. 385°; *hexamethylenetetramine*, $C_6H_{12}N_4$,T, m. p. 175°; E.p. 325°; *ψ-cumidine*, $C_6H_2Me_3\cdot NH_2$,2T, velvety-yellow needles, m. p. 183° (decomp.), E.p. 477°; *triphenylguanidine*, $NPh{:}C(NHPh)_2$,T, brilliant yellow, prismatic needles, m. p. 182°, E.p. 454°; *α-naphthyldimethylamine*. $C_{10}H_7\cdot NMe_2$,T, hard, brilliant plates, m. p. 154°, E.p. 358°; *α-naphthol*, $C_{10}H_7\cdot OH$,T, orange-yellow, silky needles, m. p. 159°, E.p. 472°; *β-naphthol*, $C_{10}H_7\cdot OH$,T, orange needles, m. p. 124°, E.p. 452°. W. S. N.

Esterification of Naphthols in Presence of Catalysts. (Miss) M. Aloe (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1921, [iii], **27**, 75—80).—The reactions of α- and β-naphthols with acetic, phenylcinnamic and benzoic anhydrides either alone or in presence of a catalyst have been investigated, the results obtained being similar to those described by Bakunin and Giordani (A., 1920, i, 543). These reactions are catalysed by ferric chloride, fuming sulphuric acid, phosphoric oxide, iodine, chlorine, and hydrochloric and hydrobromic acids.

α-Naphthyl phenylcinnamate, $C_{14}H_{11}\cdot CO_2\cdot C_{10}H_7$, forms slender, flesh-coloured needles, m. p. 119°, the *β-naphthyl* compound, being a white, pulverulent compound, beginning to become pasty at 115°, m. p. 130—145°. T. H. P.

The Mode of Action of Auxochromes. H. Kauffmann (*Annalen*, 1923, **433**, 237—241).—Whereas *o*-hydroxystilbene is colourless, its potassium salt is yellow. The latter can only possess a quinonoid structure if the potassium atom is attached to carbon; the alternative, and more probable, formula, in which the metal is bound to oxygen, is benzenoid. These facts constitute a further demonstration (cf. A., 1906, i, 577) of the incorrectness of the view that the action of auxochromes in conferring colour on benzene derivatives is to be ascribed to a quinonoid form.

[With Elisabeth Laemle.]—*o*-Hydroxystilbene is conveniently prepared by heating *o*-hydroxyphenylbenzylcarbinol at 180—200°, or, better, by boiling it with acetic anhydride; the carbinol is readily obtained by the interaction of salicylaldehyde and magnesium benzyl chloride in cold ethereal solution. *o*-Hydroxystilbene is converted by means of methyl sulphate into *o*-methoxystilbene.

The absorption curves for the phenol and its methyl ether are very similar, and only show selective absorption in the ultra-violet. The curve for the potassium salt, however, has two peaks, and shows absorption in the visible spectrum. W. S. N.

Preparation of Dihydroxyperylene. H. PEREIRA (Brit. Pat. 191363).—ββ-Dinaphthol is intimately mixed with anhydrous aluminium chloride and a basic substance such as one of the oxides or hydroxides or carbonates of the alkalis or alkaline earths, and the mixture is heated for thirty minutes at 170°. The residue is boiled with dilute hydrochloric acid and well washed. 1 : 12-Dihydroxyperylene remains in satisfactory yield. T. S. W.

Ethylene and Trimethylene Ethers of Quinol. M. KOHN and L. BENCZER (*Annalen*, 1923, **433**, 305—313; cf. Kohn and Wilhelm, A., 1923, i, 558; Kohn and Safrin, *ibid*, i, 559).—*Phenyl* p-*hydroxyphenyl ethylene ether*, $OPh{\cdot}C_2H_4{\cdot}O{\cdot}C_6H_4{\cdot}OH$, almost colourless crystals, m. p. 152—154°, is formed by boiling quinol with β-bromophenetole in concentrated aqueous solution, a concentrated solution of potassium hydroxide being gradually added. It gives a *benzoate*, leaflets, m. p. 126°, and, by the use of methyl sulphate, a *methyl ether*, m. p. 103—104°, which is also obtained when quinol methyl ether and β-bromophenetole are boiled with sodium ethoxide in alcoholic solution. Phenyl *p*-hydroxyphenyl ethylene ether reacts with a further molecule of β-bromophenetole in boiling, alcoholic sodium ethoxide solution, to give *quinol bisphenoxyethyl ether*, leaflets, m. p. 180°, which is also produced in small amount in the preparation of the original phenolic ether. The action of ethylene bromide on phenyl *p*-hydroxyphenyl ethylene ether in boiling, alcoholic sodium ethoxide solution gives *bis*-β-*phenoxy*-p-*ethoxyphenyl ethylene ether*, microscopic needles, m. p. 217°, which is also obtained by the action of diquinol ethylene ether (1 mol.) on β-bromophenetole (2 mols.) under similar conditions; the use of trimethylene bromide leads to the formation of *bis*-β-*phenoxy*-p-*ethoxyphenyl trimethylene ether*, leaflets, m. p. 174—175°, which is likewise obtained from diquinol trimethylene ether and β-bromophenetole. Quinol and phenyl γ-bromopropyl ether react in a boiling, aqueous solution containing potassium hydroxide to give *phenyl* p-*hydroxyphenyl trimethylene ether*, microscopic needles, m. p. 63°, *benzoate*, tablets, m. p. 88—90°, *methyl ether*, leaflets, m. p. 44—46°; the methoxy-derivative is also obtained by the action of quinol methyl ether and phenyl γ-bromopropyl ether in the presence of sodium ethoxide. Phenyl *p*-hydroxyphenyl trimethylene ether reacts with a second molecule of phenyl γ-bromopropyl ether in the presence of sodium ethoxide to give *quinol bisphenoxypropyl ether*, small, flat rods, m. p. 120°; if β-bromophenetole is used, the product is *quinol* β-*phenoxyethyl* γ-*phenoxypropyl ether*, leaflets, m. p. 114—115°, which is also prepared from phenyl *p*-hydroxyphenyl ethylene ether and phenyl γ-bromopropyl ether. Phenyl *p*-hydroxyphenyl trimethylene ether and ethylene bromide, or diquinol ethylene ether and phenyl γ-bromopropyl ether, react in boiling, alcoholic sodium ethoxide solution to give *bis*-γ-*phenoxy*-

p-*propoxyphenyl ethylene ether*, leaflets, m. p. 149°; under similar conditions, *p*-hydroxyphenyl trimethylene ether and trimethylene bromide, or diquinol trimethylene ether and phenyl γ-bromopropyl ether, gives *bis*-γ-*phenoxy*-p-*propoxyphenyl trimethylene ether*, needles, m. p. 147°. W. S. N.

Preparation of Diphenylene Sulphide by the Action of Sodamide on Diphenyl Sulphoxide. A. Schönberg (*Ber.*, 1923, **56**, [*B*], 2275).—Diphenyl sulphoxide, m. p. 70—71°, is readily prepared by the action of aluminium chloride on a mixture of benzene and thionyl chloride. It is transformed into diphenylene sulphide, $S<^{C_6H_4}_{C_6H_4}$, needles, m. p. 97—98°, when its solution in boiling toluene is subjected to protracted treatment with finely divided sodamide. H. W.

Derivatives of Dithioethylene and Dithioacetylene. E. Fromm and H. Landmann (*Ber.*, 1923, **56**, [*B*], 2290—2294).—A continuation of the work of Fromm, Benzinger, and Schäfer (A., 1913, i, 174) and Fromm and Siebert (A., 1922, i, 542).

Attempts to prepare dithiolethylene were unsuccessful, since dichloroethylene could not be caused to react with an alcoholic solution of sodium sulphide or sodium hydrogen sulphide, even under increased pressure. With sodium ethoxide, an explosion results owing to the evolution of chloroacetylene.

s-Diethylthiolacetylene is converted by a mixture of glacial acetic and 50% sulphuric acids into *ethylthiolacetaldehyde ethylmercaptal*, $SEt\cdot CH_2\cdot CH(SEt)_2$, a heavy, unstable liquid which is oxidised by hydrogen peroxide to *triethylsulphone-ethane*, $SO_2Et\cdot CH_2\cdot CH(SO_2Et)_2$, colourless needles, m. p. 144°; the reaction consists primarily in the addition of the elements of water with formation of the product $SEt\cdot CH_2\cdot CH(OH)\cdot SEt$, which becomes decomposed into ethyl mercaptan and the substituted aldehyde, $SEt\cdot CH_2\cdot CHO$; the products then react with one another to give the mercaptal, the yield of which can therefore be considerably improved by initial addition of a molecular proportion of ethyl mercaptan. Similarly, dibenzylthiolethylene is converted into the unstable *benzylmercaptal* of *benzylthiolacetaldehyde*, which is oxidised by potassium permanganate to αβ-*dibenzylsulphone*-α-*benzylthiolethane*, $CH_2Ph\cdot SO_2\cdot CH(S\cdot CH_2Ph)\cdot SO_2\cdot CH_2Ph$, m. p. 142°, and by hydrogen peroxide (30%) to *tribenzylsulphone-ethane*, $CH_2Ph\cdot SO_2\cdot CH_2\cdot CH(SO_2\cdot CH_2Ph)_2$, lustrous leaflets, m. p. 261°. The sulphone-sulphide is reduced by zinc dust and glacial acetic acid to dibenzylsulphone-ethane, m. p. 304°, which is also obtained (together with benzyl mercaptan) from the trisulphone.

Diethylsulphone-ethylene, $SO_2Et\cdot CH{:}CH\cdot SO_2Et$, slender needles, m. p. 88°, is prepared by the oxidation of diethylthiolethylene with hydrogen peroxide; it is reduced by zinc dust and acetic acid to diethylsulphone-ethane, m. p. 137°. Dibenzyldithiolethylene is oxidised by potassium permanganate to α-*benzylthiol*-β-*benzylsulphone-ethylene*, $CH_2Ph\cdot S\cdot CH{:}CH\cdot SO_2\cdot CH_2Ph$, lustrous needles, m. p. 127°, which is not affected by zinc dust and acetic acid, and

by hydrogen peroxide to *dibenzylsulphone-ethylene*, colourless needles, m. p. 167°, which is reduced to dibenzylsulphone-ethane, m. p. 304°.

The presence of the conjugated double bonds in dibenzylsulphone-ethylene causes it to react with phenylhydrazine, with the ultimate production of the *phenylhydrazone* of *benzylsulphonacetaldehyde*, $CH_2Ph{\cdot}SO_2{\cdot}CH_2{\cdot}CH{:}N{\cdot}NHPh$, pale yellow crystals, m. p. 139—140°, and the *phenylhydrazine* salt of benzylsulphinic acid, lustrous leaflets, m. p. 181°.

Although dibenzylsulphone-ethylene readily unites with hydrogen, it does not appear possible to add the elements of water. On the other hand, α-benzylthiol-β-benzylsulphone-ethylene, which cannot be reduced, readily combines with water to form the *benzylmercaptal* of *benzylsulphonacetaldehyde*, $CH_2Ph{\cdot}SO_2{\cdot}CH_2{\cdot}CH(SO_2{\cdot}CH_2Ph)_2$, slender needles, m. p. 81°, which is oxidised by hydrogen peroxide to tribenzylsulphone-ethane, m. p. 261°.

Dibenzylthiolacetylene is oxidised by hydrogen peroxide at the atmospheric temperature to *dibenzylsulphone-acetylene*, $CH_2Ph{\cdot}SO_2{\cdot}C{:}C{\cdot}SO_2{\cdot}CH_2Ph$, lustrous leaflets, m. p. 212°; on account of the instability of the material, it has not been found possible to add the elements of water.

s-Tetrachloroethane and sodium benzylmercaptide give *tetrabenzylthiolethane*, crystals, m. p. 63°, which is oxidised by hydrogen peroxide in the presence of glacial acetic acid to *tetrabenzylsulphone-ethane*, lustrous leaflets, m. p. 203°. H. W.

Catalytic Dehydration of Hydroaromatic Alcohols. J. B. Senderens (*Compt. rend.*, 1923, **177**, 1183—1186).—*cyclo*Hexanol, when distilled with 3% of its weight of sulphuric acid trihydrate, gives a 92% yield of *cyclo*hexene, the production of which depends on its steady removal from the reaction mixture; practically none is formed simply by heating under reflux. *cyclo*Hexane-1 : 2-diol is very little affected by sulphuric acid trihydrate, about 20% being converted into condensed hydrocarbons. Concentrated sulphuric acid at 110° affords a resin and a little $\Delta^{1:3}$-*cyclo*hexadiene. *cyclo*Hexane-1 : 3-diol is readily converted by the trihydrate at 130—145° into $\Delta^{1:3}$- and $\Delta^{1:4}$-*cyclo*hexadienes, *cyclo*hexane-1 : 4-diol, under similar conditions, affording $\Delta^{1:3}$-*cyclo*hexadiene. E. E. T.

Halochromic Phenomena with Phenylethinylcarbinols. W. Weltzien, F. Micheel, and K. Hess (*Annalen*, 1923, **433**, 247—267).—It has already been shown that certain arylethinylcarbinols, a quinonoid rearrangement of which is highly improbable, are, as regards halochromy, in every way similar to carbinols, including radicles of the triphenylmethyl type containing so-called tervalent carbon (Hess and Weltzien, A., 1922, i, 35). Trianisylethinylcarbinol, and phenylethinyldianisylethinylcarbinol have now been prepared by the method previously employed, and shown to behave in the same way. This confirms the previous conclusion, that in derivatives of triphenylmethane exhibiting halochromy, this property is not destroyed by replacing the phenyl groups by "gap-linkings."

A better method for preparing *p*-methoxyphenylacetylene than

that given by Manchot (A., 1912, i, 230) is as follows. Anisaldehyde and ethyl acetate are condensed by means of sodium to ethyl *p*-methoxycinnamate, the dibromide of which is hydrolysed by boiling for four hours with alcoholic potassium hydroxide solution, to give *p*-methoxyphenylpropiolic acid, the copper salt of which is decomposed by the action of steam to give the required product.

The action of thionyl chloride on sodium *p*-methoxyphenylpropiolate in ethereal suspension at −20° gives p-*methoxyphenylpropiolyl chloride*, small, slightly yellow needles, m. p. 43°, which is treated in ethyl chloride solution at −20° with two equivalents of magnesium *p*-methoxyphenylethinyl bromide, prepared in ethereal solution from ethyl bromide and *p*-methoxyphenylacetylene; the product is *trianisylethinylcarbinol*, $OH\cdot C(C{\equiv}C\cdot C_6H_4\cdot OMe)_3$, an amorphous, slightly brown powder, which darkens on keeping, and sinters and melts at 55—60°. It is reduced in absolute alcoholic solution by means of platinum black and hydrogen, to give *trianisylethylcarbinol*, small, fragile, snow-white needles, m. p. 74°.

Phenylethinyldianisylethinylcarbinol, $OH\cdot C(C{\equiv}C\cdot C_6H_4\cdot OMe)_2\cdot C{\equiv}CPh$, a brown powder, is obtained by the interaction of phenylpropiolyl chloride (1 mol.) and magnesium *p*-methoxyphenylethinyl bromide (4 mols.) in ethereal solution at −20°.

The halochromy of these and other carbinols is investigated at −78° in solutions in various inert solvents. Trianisylethinylcarbinol gives a *perchlorate*, $(OMe\cdot C_6H_4\cdot C{\equiv}C)_3C\cdot ClO_4\ldots HClO_4$, an explosive powder having a green lustre, which is deep blue in solution, but the perchlorates of diphenylphenylethinylcarbinol and triphenylethinylcarbinol are too soluble to be isolated. Trianisylethinylcarbinol gives an insoluble, dark blue *sulphate*, and a deep blue *hydrochloride*, which has a green lustre, and decomposes at the ordinary temperature with evolution of hydrogen chloride. With sulphuric acid or hydrochloric acid, phenylethinyldianisylethinylcarbinol and phenyldianisylcarbinol give, respectively, blue and orange-red colorations. Additive *compounds* with *stannic chloride* are as follows: triphenylcarbinol, orange-yellow, $CPh_3\cdot OH\ldots 2SnCl_4$, which gradually loses hydrogen chloride and stannic chloride when kept at the ordinary temperature in a vacuum; trianisylcarbinol, phenyldianisylcarbinol, or diphenylphenylethinylcarbinol, orange-red; triphenylethinylcarbinol, dark violet, and trianisylethinylcarbinol, bluish-violet, which pass, when kept in a vacuum, to substances of the composition $C(C{\equiv}C\cdot R)_3\cdot O\cdot SnCl_3$. Trianisylethinylcarbinol, phenyldianisylethinylcarbinol, triphenylethinylcarbinol, phenyldiphenylethinylcarbinol, and diphenylphenylethinylcarbinol do not give coloured solutions in trichloroacetic acid or liquid sulphur dioxide, but the first gives a dark blue, and the second a blue, solution in nitric acid.

Diphenylphenylethinylcarbinol may be recovered quantitatively from its dark orange-red solution in concentrated sulphuric acid by neutralising by means of ammonia; but if the solution is kept until it is yellow, phenyl phenylstyryl ketone is obtained. Triphenylethinylcarbinol may also be recovered from its solution in sulphuric acid, but not trianisylethinylcarbinol, which evidently

undergoes transformation very readily; but the first experiment shows that the halochromic phenomena are given by the untransformed material. Moreover, both the last-mentioned compounds, and also triphenylcarbinol, may be recovered by decomposing the double tin salts at −78° by the gradual addition of moist acetone to its solution in chloroform and ethyl chloride.

Straus and Dützmann (A., 1922, i, 148) have found that the addition of groups to derivatives of chlorodiphenylmethane influence the intensity but not the depth of the colour. The same conclusion is now drawn with regard to the carbinols investigated, any of which, with different solvents, gives either a colourless solution, or solutions having the same shade of colour, although of varying intensity.

Objection is taken to the view of Skraup and Freundlich (A., 1923, i, 667), that the halochromy of unsaturated ketones with acids or metallic halides is a reaction of the ethylene linking, because exactly the same type of additive compound with stannic chloride, $2X...SnCl_4$, is formed by a great number of alcohols and ketones, quite irrespective of whether they are saturated or not, or of the extent to which they are unsaturated. W. S. N.

Formation of αβ-Ketone-alcohols (Acyloins) and αβ-Diketones by the Action of Alkali Metals on Aliphatic Esters. H. Scheibler and F. Emden (*Annalen*, 1923, **434**, 265—284).—(1) *Mechanism of the Reaction during the Synthesis of Acyloins.*—The mechanism suggested by Bouveault and Locquin (A., 1906, i, 782) is difficult to reconcile with the mechanism of ethyl acetoacetate formation. It is now shown that the same compound, $CH_2{:}C(ONa)\cdot OEt$, may be initially formed in both syntheses. In the ethyl acetoacetate synthesis, each molecule of the initial compound at once reacts with ethyl acetate (present in excess), but in presence of a solvent and with deficiency of ethyl acetate, this second process is delayed, hydrogenation occurring instead :

$$2CR_2{:}C(ONa)\cdot OEt+2H=CHR_2\cdot C(ONa)(OEt)\cdot C(ONa)\cdot OEt\cdot CHR_2.$$

The latter compound then reacts with the excess of sodium present, as follows : $CHR_2\cdot C(ONa)(OEt)\cdot C(ONa)(OEt)CHR_2+2Na=2H+2EtONa+CR_2{:}C(ONa)\cdot C(ONa){:}CR_2$ $CR_2{:}C(ONa)\cdot C(ONa){:}CR_2+2H=CHR_2\cdot C(ONa){:}C(ONa)CHR_2$, the product being the disodium derivative of acyloin in the case of ethyl acetate. In some cases (cf. Scheibler, Ziegner, and Peffer, A., 1923, i, 82) hydrogenation is more profound.

Ethyl αα-dimethylpropionate and benzoate, which are incapable of affording enolic derivatives, are very slowly converted by sodium, in ethereal solution, into αβ-ketone alcohols, unaccompanied, however, by αβ-diketones. Metal ketyls are probably the intermediaries in such processes :

$$Ph\cdot CO_2Et \xrightarrow{Na} CPh(OEt)\cdot ONa \ldots \longrightarrow CPhNa(OEt)\cdot ONa \longrightarrow EtONa+{:}CPh(ONa) \longrightarrow ONa\cdot CPh{:}CPh\cdot ONa$$

(2) *Autoxidation of Endiolates.*—The disodium (or dipotassium) derivatives of the type, $CHR_2\cdot C(ONa){:}C(ONa)CHR_2$, on decom-

position with water, afford acyloins, but if the experiment is carried out without excluding oxygen, autoxidation of the metal derivative (for which the name *endiolate* is proposed) occurs, an αβ-diketone resulting. Occasionally, a benzil–benzilic acid change also occurs, *e.g.*, with the potassium derivative from ethyl *iso*butyrate, when α-hydroxy-β-methyl-α-*iso*propylbutyric acid results. The endiolates, which are highly coloured, react with ethyl bromide (cf. Bouveault and Locquin, *loc. cit.*) to give the corresponding *O*-ethers. The di-potassium derivative of pyrocatechol may be regarded as an endiolate, when its autoxidation falls into line with that of the compounds under discussion.

Ethyl dibenzylacetate (1 mol.) when left in ethereal solution over powdered sodium (2 atoms), in absence of air, affords a yellow product which, on decomposition with water, gives (83% yield) *tetrabenzylacetoin* (*γ-hydroxy-ααδδ-tetrabenzylbutane-β-one*), colourless leaflets, m. p. 148—149°, together with a little *ααδδ-tetrabenzylbutane-βγ-dione*, yellow needles, m. p. 121—122°. The former substance does not react with hydroxylamine or with phenylhydrazine. When potassium is substituted for sodium in the above preparation, a red reaction mixture is obtained (affording the same decomposition products as before) and this, on treating with ethyl bromide, gives *βγ-diethoxy-ααδδ-tetrabenzyl-Δ$^{\beta}$-butene* (m. p. 158°), which does not respond to bromine or permanganate tests for unsaturation, and is unaffected by prolonged heating with aqueous hydrobromic acid or alcoholic potassium hydroxide. A mixture of hydriodic acid and phenol effects the conversion of the diethoxy- into the dihydroxy-compound.

The above diketone is readily obtained (1) by aërating the reaction mixture (affording otherwise the acetoin), or (2) by the action of nitric acid on the acetoin. The diketone does not react with hydroxylamine, phenylhydrazine, or *m*-tolylenediamine. Hydrogen peroxide converts it, quantitatively, into dibenzylacetic acid, whilst on fusion with alkali it is partly converted into the acetoin. The moist ethereal solution is rapidly decolorised in sunlight, with formation of the acetoin, the original colour reappearing on excluding light. A yellow oil probably containing an aldehyde, b. p. 160—200°, is formed in this process.

Sodamide converts ethyl dibenzylacetate into a mixture of dibenzylacetamide and *tetrabenzyldiacetamide* (m. p. 172—173°).

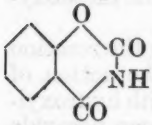
By the action of sodium or potassium on various esters, with or without admission of air, various acyloins, etc., have been obtained in an impure state: *δ-hydroxy-αη-diphenyl-αη-dimethylhexane-γ-one* (from ethyl β-phenyl-α-methylpropionate) has b. p. 225—235°/25 mm.; *δ-hydroxy-αη-diphenylhexane-γ-one* (from ethyl β-phenylpropionate) has b. p. 240—265°/38 mm.; and *αη-diphenyl-αη-dimethylhexane-γδ-dione* has b. p. 225—230°/27 mm. E. E. T.

The Action of Nitric Acid on Naphthalic Anhydride. M. A. Mihăilescu and A. Steopoe (*Bull. Acad. Sci. Roumaine*, 1923, **8**, 102—110).—Contrary to statements in the literature, naphthalic anhydride can be nitrated by nitric acid, the progress of the reaction

depending on the concentration of acid, duration of boiling, and the amount of nitrous acid present. Some oxidation may also occur. The best results are obtained by boiling naphthalic anhydride with fuming nitric acid (*d* 1·47), when there is obtained a mixture of 3-nitronaphthalic anhydride, m. p. 251—252° (other authors give 247—249°) and a *dinitronaphthalic anhydride*, yellow needles, m. p. 207—208°. There is also obtained a small quantity of an unknown substance, m. p. 175° (decomp.), giving a red coloration with alkali; some resin is also formed. Naphthalic anhydride, or its nitro-compounds, should not be recrystallised from nitric acid, as recommended by others, but from acetic acid. E. H. R.

Action of "Aspirin" on Urethane. E. Comanducci (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1921, [iii], **27**, 48—52).—At the ordinary temperature, urethane and *o*-acetoxybenzoic acid do not react, but when heated together they give rise to products varying with the proportions of the compounds taken. The reaction commences at about 90°, ethyl acetate and salicylurethane being formed, $CO_2H\cdot C_6H_4\cdot OAc+NH_2\cdot CO\cdot OEt=CO_2H\cdot C_6H_4\cdot O\cdot CO\cdot NH_2+CH_3\cdot CO_2Et$. At a temperature exceeding 130°, the mass turns yellow, with formation of acetic acid and a little ethyl acetate, whilst at 180—182° carbon dioxide and ammonia are produced and at about 200° phenol, salicylamide, the nitrile of salicylic acid, and carbonylsalicylamide.

Salicylurethane forms white crystals, m. p. 113°; *salicylamide*, $OH\cdot C_6H_4\cdot CO\cdot NH_2$, forms yellow leaflets, m. p. 133°, and in aqueous or alcoholic solution gives an intense violet coloration with ferric chloride; the *nitrile* of *salicylic acid*, $(OH\cdot C_6H_4\cdot CN)_x$, is a yellow compound, m. p. 280°. *Carbonylsalicylamide* (annexed formula), forms straw-yellow laminæ, m. p. 221°, and in alcoholic solution gives a pink coloration with ferric chloride. T. H. P.



Addition to Compounds with Marked Conjugation. II. Addition of Hydrogen and Bromine to Cinnamylidene Derivatives. K. von Auwers and W. Müller (*Annalen*, 1923, **434**, 165—184).—Cinnamylidene derivatives are studied in a similar manner to that used in the case of analogous aliphatic acids (this vol., i, 8). Cinnamylideneacetic acid gives an αβ-dibromide, crotonylidene- and cinnamylidene-malonic esters giving γδ-dibromides.

Reduction of cinnamylidenemalonic acid (cf. Thiele and Meisenheimer, A., 1899, i, 603) gives, besides the αδ-dihydro-acid (*anilide*, m. p. 83—85°), *δ-phenyl-γ-valerolactone-α-carboxylic acid*, yellow crystals, m. p. 123—124° (with loss of carbon dioxide). The latter acid on heating, gives δ-phenyl-γ-valerolactone, whilst the lactonic acid is also formed by treating the above αδ-dihydro-acid successively with hydrogen bromide and water.

Cinnamylideneacetic acid and bromine afford a mixture of cis-*α-bromocinnamylideneacetic acid* (m. p. 182—183°; *methyl* ester, m. p. 60—61°), and *β-bromo-γ-benzylidenebutyric acid*, m. p. 135—136°. The latter, on ozonolysis, affords benzaldehyde, and on treatment with sodium carbonate gives a mixture of cinnamylideneacetic acid

and phenylbutadiene. The above *cis*-acid is best obtained from the cinnamylideneacetic acid–bromine mixture by the action of sodium acetate.

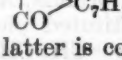
The last-mentioned mixture, which at the outset contains little but *αβ-dibromo-γ-benzylidenebutyric acid*, on ozonolysis (before secondary reactions set in) and subsequent treatment of the product with semicarbazide, gives a mixture of the semicarbazones of benzaldehyde and of *bromofumaric* (*maleic*?) *semialdehyde* (m. p. 247°), together with a small quantity of a substance (m. p. 248—250)° which is probably *β-bromoacraldehyde semicarbazone*. *α-Bromoacraldehyde semicarbazone*, prepared for comparison, decomposes at 160°.

Methyl cinnamylideneacetate with bromine affords *methyl αβ-dibromo-γ-benzylidenebutyrate* (m. p. 80—81°), which with cold sodium hydroxide, followed by the hot alcoholic reagent, is converted into trans-*α-bromocinnamylideneacetic acid* (m. p. 194°), this being convertible into the methyl ester, and obtainable again therefrom without change of configuration. Ozonolysis of the ester of m. p. 80—81° gives, after treating the product with semicarbazide, a mixture of benzoic acid, benzaldehyde semicarbazone, the above semicarbazone melting at 247°, and the corresponding *methyl* ester, $NH_2{\cdot}CO{\cdot}NH{\cdot}N{:}CH{\cdot}CH{:}CBr{\cdot}CO_2Me$, m. p. 214—215°. The dibromo-ester (m. p. 80—81°), with bromine in sunlight, gives αβγδ-tetrabromo-δ-phenylbutyric acid.

The γδ-dibromide of methyl cinnamylidenemalonate, on treatment with potassium acetate, gives *methyl γ-bromocinnamylidenemalonate* (m. p. 86·5—88·5°), which on ozonolysis affords benzoic, oxalic, and mesoxalic acids, the latter being identified as the p-*nitrophenylhydrazone*, m. p. 202°.

γ-Bromo-β-hydroxy-γ-benzylidenebutyric acid (from malonic acid, α-bromocinnamaldehyde, and pyridine) has m. p. 113—114°, and is converted by hydrochloric acid into *γ-bromocinnamylideneacetic acid*, m. p. 137·5—138·5°, which forms *methyl* and *ethyl* esters melting, respectively, at 59—60° and 56—57°, and with bromine affords *αβγ-tribromo-γ-benzylidenebutyric acid* (m. p. 146—147°). The latter acid, on ozonolysis, gives benzaldehyde as the only recognisable product. E. E. T.

Molecular Rearrangements of the Camphor Series. XIV. Structure of *iso*Campholactone. P. K. Porter and W. A. Noyes (*J. Amer. Chem. Soc.*, 1923, **45**, 2366—2373).—The following proof is offered that *iso*campholactone (Noyes, A., 1895, i, 295, 552) is the lactone of 3-hydroxy-1 : 2 : 3-trimethyl*cyclo*pentane-1-carboxylic acid.

When it is oxidised by means of nitric acid, there are formed nitro*iso*campholactone and a lactonic acid,  (Noyes and Homberger, A., 1911, i, 110). The latter is converted successively into the disodium and the *disilver* salts of the hydroxydicarboxylic acid; the disilver salt is transformed by means of ethereal methyl iodide into the *dimethyl* ester, b. p. 156—160°/25

mm., which is only very slightly attacked by the action of Beckmann's chromic acid mixture, even after keeping for twelve hours. Hence the hydroxyl group is tertiary. The lactonic acid is converted by heating with phosphorus pentachloride into the acid chloride, which is not isolated, but is treated in dry ethereal solution with cold concentrated ammonia solution (*d* 0·9), whereby an *amide*, m. p. 162—163°, is obtained. The action of cold sodium hypobromite solution on the amide gives an oily *keto-acid* (*barium* salt, $+2H_2O$), from which it follows that the amide and hydroxyl radicles are attached to the same carbon atom. This keto-acid reacts in ethereal solution with magnesium methyl iodide to give *iso*campholactone, and a small quantity of an *acid*, m. p. 96—97°, $[\alpha]_D^{28}$ −37·5° (in alcohol), probably the *trans*-hydroxydicarboxylic acid. These reactions can only be explained if *iso*campholactone has the structure suggested, whilst the lactonic acid formed from it by oxidation is the lactone of 3-hydroxy-1 : 2-dimethyl*cyclo*pentane-1 : 2-dicarboxylic acid. The amide is then the 3-amide of this acid, and the keto-acid is 1 : 2-dimethyl*cyclo*pentan-3-one-1-carboxylic acid.

It is considered probable that the 2-methyl group in *iso*campholactone is in the *trans*-position with respect to the other two methyl groups, whilst in campholactone all three lie in the same plane.

Nitro*iso*campholactone, which presumably has the nitro-group in the position 2, is converted almost quantitatively, on treatment with warm 2*N*-sodium hydroxide solution, into acetone and 2-*nitro*-1-*methyl*cyclo*butane*-1-*carboxylic acid*, m. p. 70—72°, $[\alpha]_{435}^{26}$ −246·81°, $[\alpha]_{546\cdot1}^{25}$ −119·3°, $[\alpha]_{578}^{25}$ −101·51°, $[\alpha]_D^{25}$ −87·31°, *barium* salt, needles, *silver* salt, *methyl* ester, b. p. 120—125°/5 mm. (slight decomp.), $[\alpha]_{546\cdot1}^{25}$ −93·2°, $[\alpha]_{578\cdot7}^{25}$ −80·2°, d^{20} 1·16907, n 1·4416. The *amide*, m. p. 94—95°, is obtained by decomposing nitro*iso*campholactone by means of concentrated ammonia solution. The acid, its amide, or its methyl ester gives a blue coloration with nitrous acid, which demonstrates the presence of a secondary nitro-group and a *cyclo*butane ring, rather than a tertiary nitro-group and a *cyclo*propane ring. This conclusion is supported by the fact that the amide gives a *sodium* salt, which is hydrolysed to the *cyclo*butane acid by means of dilute sulphuric acid or of sodium hydroxide solution; with the latter reagent, a blue coloration is produced, and nitrous oxide is evolved. Similarly, the methyl ester gives a *sodium* salt, which gives a blue solution when hydrolysed by means of dilute sulphuric acid, nitrous oxide being generated. W. S. N.

Preparation of Mixed Esters of Phthalic Acid. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 371046; from *Chem. Zentr.*, 1923, iv, 538).—Basic mixed esters of phthalic acid of the general formula, Aryl·$(CO_2R)^1$·$(CO_2R')^2$, where aryl denotes phenyl or substituted phenyl, R=alkyl, and R′=an alkylamine group such as $-CH_2\cdot CH_2\cdot N(Alkyl)_2$, are prepared by the action of a phthalic ester chloride on an alkylamine, or of a hydrogen phthalate on a halogenalkyldialkylamine. *Methyl diethylaminoethyl*

phthalate, $CO_2Me{\cdot}C_6H_4{\cdot}CO_2{\cdot}[CH_2]_2{\cdot}NEt_2$, is prepared from methyl phthalate chloride and diethylaminoethanol; it is a yellow oil; the *hydrochloride* has m. p. 114°. *Benzyl diethylaminoethyl phthalate*, from benzyl hydrogen phthalate and chloroethyl diethylamine, is a light yellow oil. *Ethyl diethylaminoethyl 3 : 6-dichlorophthalate*, $CO_2Et{\cdot}C_6H_2Cl_2{\cdot}CO_2{\cdot}[CH_2]_2{\cdot}NEt_2$, from chloroethyldiethylamine and ethyl hydrogen 3 : 6-dichlorophthalate, is a light yellow oil; the *hydrochloride* has m. p. 165°. *Methyl dimethylaminoethyl phthalate* is a yellow oil; the *hydrochloride* has m. p. 103°. G. W. R.

Some Derivatives of Deoxycholic Acid. J. Pascual Vila (*Anal. Fis. Quím.*, 1923, **21**, 397—400).—*Methyl deoxycholate* prepared by esterification of deoxycholic acid, forms needles, m. p. 75—78°. By the action on it of gaseous carbonyl chloride, a *chloroformate*, $OH{\cdot}C_{23}H_{37}(O{\cdot}COCl){\cdot}CO_2Me$, crystals, m. p. 138—139°, is obtained. By heating this at 140°, *methyl chlorohydroxycholanate*, $OH{\cdot}C_{23}H_{37}Cl{\cdot}CO_2Me$, needles, m. p. 121—122°, is obtained. G. W. R.

Preparation of an *iso*Deoxycholic Acid. J. Pascual Vila (*Anal. Fis. Quím.*, 1923, **21**, 390—396; cf. Boedecker and Volk, A., 1922, i, 1027).—An *iso*deoxycholic acid was prepared by the author by the following method. Methyl cholate is treated with a current of carbonyl chloride, whereby a chloroformic ester, having the composition $C_{23}H_{36}(OH)_2(O{\cdot}COCl){\cdot}CO_2Me$ is obtained. It is crystalline and has m. p. 140—141° (decomp.). This compound is heated above its melting point and the product treated with sodium ethoxide in ethyl-alcoholic solution, whereby *chlorodihydroxycholanic acid*, $C_{23}H_{36}Cl(OH)_2{\cdot}CO_2H$, is obtained, having m. p. 196—197°. Treatment of this compound with sodium amyloxide yields *dihydroxycholenic acid*, $C_{23}H_{35}(OH)_2{\cdot}CO_2H$, which is obtained in two forms, namely, large prisms or needles, m. p. 216—217°, and needles, m. p. 181°. Hydrogenation of the product having m. p. 216—217° in the presence of palladium yields β-iso*deoxycholic acid*, $C_{23}H_{37}(OH)_2{\cdot}CO_2H$, m. p. 226—227°. The constitution of these compounds is discussed. G. W. R.

Hyoglycodeoxycholic Acid and Hyodeoxycholic Acid. A. Windaus and A. Bohne (*Annalen*, 1923, **433**, 278—287).—A preliminary account of this work has already appeared (A., 1923, i, 922).

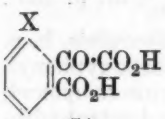
Hyodeoxycholic acid, small, four-sided leaflets, m. p. 196—197° (potassium salt, slender needles), is obtained by the action of 15% potassium hydroxide solution at 135° on the sodium salt of hyoglycodeoxycholic acid, hexagonal leaflets, m. p. 215—216° (from glacial acetic acid or ethyl acetate), or m. p. 150—151° (from aqueous alcohol), *methyl* ester, small, elongated leaflets, m. p. 215—216°. It is oxidised by means of chromic anhydride in cold glacial acetic acid–concentrated sulphuric acid solution, to *dehydro-*

hyodeoxycholic acid, $C_{24}H_{36}O_4,2H_2O$, m. p. 203—204°, $+H_2O$, four-sided leaflets, m. p. 161·5—162° (*disemicarbazone*, indefinite crystals, *methyl* ester, small leaflets, m. p. 139°, *ethyl* ester, spangles, m. p. 140°). This diketo-acid is reduced by means of zinc amalgam in boiling, glacial acetic acid–concentrated hydrochloric acid solution to hyocholanic acid, leaflets, m. p. 162°, which is identical with the acid, $C_{24}H_{40}O_2$, obtained by Windaus and Neukirchen (A., 1920, i, 41) from cholestan, and gives the following esters: *methyl*, small prisms or leaflets, m. p. 90—91°; *ethyl*, glistening leaflets, m. p. 84°; *propyl*, slender needles, m. p. 101°; n-*butyl*, fan-shaped aggregates, m. p. 87°. *Propyl cholanate*, prisms, has m. p. 56—57°; *butyl cholanate*, prisms, has m. p. 53°. When hyodeoxycholic acid is heated at 320—340° under 15 mm. pressure, 2 mols. of water are eliminated, with formation of *hyocholadienic acid*, $C_{24}H_{36}O_2$, rosettes of small, slender needles, sinters at 135°, m. p. 142°. The reduction of this unsaturated acid in glacial acetic acid solution by means of palladium black and hydrogen gives a mixture, m. p. 142° (indefinite), of cholanic and hyocholanic acids, in contrast with the behaviour of the diketo-acid (above), which gives exclusively hyocholanic acid. Evidently the asymmetry of the carbon atom 5 (cf. A., 1923, i, 922) is lost in the unsaturated acid, which can only mean that there is a double bond between the atoms 5 and 4, or 5 and 6. Hence one of the two hydroxyl groups in hyodeoxycholic acid is attacked in the position 4 or 6. W. S. N.

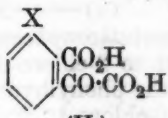
Syntheses of Dibasic Acids derived from Ethers. M. Godchot (*Compt. rend.*, 1923, **177**, 1224—1226).—*Ethyl* αα-*diphenyldiglycollate*, $CO_2Et{\cdot}CHPh{\cdot}O{\cdot}CHPh{\cdot}CO_2Et$ (from the sodium derivative of ethyl phenylglycollate and ethyl α-bromophenylacetate), on hydrolysis affords the corresponding *acid*, needles, decomposing without melting at 300°. *Ethyl* α-*phenyl*-α′-*methyldiglycollate* (from the sodium derivative of ethyl phenylglycollate and ethyl α-bromopropionate), has b. p. 180—190°/15 mm. (with some decomposition), the *acid* (needles) having m. p. 188°. *Ethyl* α-*phenyldiglycollate* (from the sodium derivative of ethyl phenylglycollate and ethyl chloroacetate) has b. p. 182—184°/10 mm., d^{21} 1·127, n_D^{21} 1·4925. The corresponding *acid* is a syrup, b. p. 203°/15 mm. (slight decomposition). The *diamide* (from the ester and ammonia) melts at 159—160°. E. E. T.

Benzo-polymethylene Compounds. X. Oxidative Degradation of Tetrahydronaphthalene and Substituted Tetrahydronaphthalenes to Phthalonic Acid and Phthalic Acids. J. von Braun [with O. Braunsdorf, P. Engelbertz, E. Hahn, G. Hahn, O. Hainbach, W. Kredel, and K. Larbig] (*Ber.*, 1923, **56**, [*B*], 2332—2343).—Phthalonic acid may be prepared by the oxidation of naphthalene by alkaline permanganate, but the process suffers from the drawbacks that it can only be applied with very dilute solutions, and the product is contaminated with phthalic acid. Tetrahydronaphthalene, on the other hand, can be almost quantitatively oxidised to phthalonic acid in the presence of very

small volumes of liquid. *ar*-Substituted tetrahydronaphthalenes can be similarly converted into mixtures of the two possible phthalonic acids (cf. annexed formulæ, I and II), the separation of which from one another is scarcely possible when the substituent is in the β-position, but much easier when it is in the α-position; in the latter case, the isomerides are frequently formed in very unequal amount and, also, an acid of type I is converted by alcohol and hydrogen chloride into the normal ester, whereas a compound of type II yields the hydrogen ester under these conditions. All substituted phthalonic acids resemble the parent acid in their ready oxidisability by permanganate in acid solution. Since the isomerides I and II yield the same phthalic acids, the preparation of the latter can be effected far more advantageously by two successive actions from substituted tetrahydronaphthalenes than from substituted naphthalenes.



(I.)



(II.)

Phthalonic acid is readily prepared by the addition of the requisite quantity of finely-divided permanganate to a hot mixture of 1 : 2 : 3 : 4-tetrahydronaphthalene and water. If the reagents are mixed in the reverse order, the oxidation almost invariably proceeds too far, with the production of phthalic acid. The latter substance is very easily prepared by the oxidation of tetrahydronaphthalene in alkaline solution, removal of the manganese dioxide, acidification of the solution, and further oxidation by permanganate.

6-Nitro-1 : 2 : 3 : 4-tetrahydronaphthalene is converted successively into a mixture of nitrophthalonic acids and 4-nitrophthalic acid, m. p. 160°. 5-Nitro-1 : 2 : 3 : 4-tetrahydronaphthalene yields *2-nitro-6-carboxyphenylglyoxylic acid* mixed with smaller quantities of *3-nitro-2-carboxyphenylglyoxylic acid* and traces of 3-nitrophthalic acid. The acid first named is conveniently purified through its sparingly soluble *barium* salt ($+5H_2O$). It has m. p. 185°; the *hemihydrate* is also described. The *ammonium* salt ($+8H_2O$), the *sodium* salt ($+2H_2O$), and the *diethyl* ester, m. p. 65—66°, are prepared. The isomeric 3-nitro-2-carboxyphenylglyoxylic acid ($+H_2O$) has m. p. 191°. The mixture of 5- and 6-nitro-1 : 2 : 3 : 4-tetrahydronaphthalenes (obtained by the mono-nitration of the hydrocarbon) is transformed by successive oxidation in alkaline and acid solution into a mixture of nitrophthalic acids which, when esterified, gives a mixture of ethyl 4-nitrophthalate, m. p. 35°, b. p. 213°/17 mm., and ethyl hydrogen 3-nitrophthalate, m. p. 111°. Hydrolysis of the ester gives the two nitrophthalic acids in the homogeneous condition.

5-Chloro-1 : 2 : 3 : 4-tetrahydronaphthalene, a colourless liquid, b. p. 115—116°/12 mm., is prepared in somewhat unsatisfactory yield from the corresponding amine. It is converted by permanganate in alkaline solution into a mixture of acids which are separated by the esterification method. The hydrogen esters are hydrolysed to 3-chlorophthalic acid and 3-chloro-2-carboxyphenylglyoxylic acid, which is isolated in the form of its condensation

product with phenylhydrazine, $C_6H_3Cl<\begin{matrix}C(CO_2H):N\\ |\\ CO\text{———}NPh\end{matrix}$, m. p. 155°. The neutral ester is *ethyl* 2-*chloro*-6-*carbethoxyphenylglyoxylate*, b. p. 195—197°/13 mm.; it is hydrolysed to 2-chloro-6-carboxyphenylglyoxylic acid, which is analysed as the phenylhydrazine *compound*, m. p. 215°. The mixture of 5- and 6-chloro-1 : 2 : 3 : 4-tetrahydronaphthalenes, b. p. 117—130°/17 mm., obtained by the chlorination of the hydrocarbon at 10° in the presence of iodine, gives a mixture of chlorophthalic acids in about 70% yield. Separation is effected by esterification. *Ethyl* 4-*chlorophthalate* is a colourless liquid, b. p. 173—174°/16 mm., which is hydrolysed to 4-chlorophthalic acid, m. p. 157°. *Ethyl hydrogen* 3-*chlorophthalate* crystallises in coarse prisms, m. p. 118—119°, and gives 3-chlorophthalic acid, m. p. 186—187°; the *imide*, m. p. 233°, and the *chloride*, b. p. 169—171°/16 mm., of the latter are described.

5 : 6 : 7 : 8-*Tetrachloro*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m. p. 172°, b. p. 180°/26 mm., is readily prepared by exhaustive chlorination of tetrahydronaphthalene in diffuse daylight. It is converted by bromine in the presence of boiling carbon disulphide into a *dibromide* (presumably an αβ-disubstituted compound), m. p. 142°, which is transformed by sodium ethoxide into tetrachloronaphthalene, m. p. 198°.

5-Bromo-1 : 2 : 3 : 4-tetrahydronaphthalene (cf. Smith, T., 1904, **85**, 728) is similarly oxidised to a mixture of 3-bromophthalic acid, 2-bromo-6-carboxyphenylglyoxylic acid, and 3-bromo-2-carboxyphenylglyoxylic acid. The substituted glyoxylic acids could not be isolated in a homogeneous condition. *Ethyl* 2-*bromo*-6-*carboxyphenylglyoxylate* has b. p. 202—206°/13 mm. Successive oxidation of the mixture of α- and β-bromotetrahydronaphthalenes in alkaline and acid solution gives 4-*bromophthalic acid*, m. p. 171—172° (*ethyl* ester, b. p. 190—191°/16 mm.), and 3-bromophthalic acid, m. p. 188° (*ethyl hydrogen* ester, needles, m. p. 127—128°).

5-Sulphonamido-1 : 2 : 3 : 4-tetrahydronaphthalene is readily converted into 2-*sulphonamido*-4-*carboxyphenylglyoxylic acid*, lustrous leaflets, m. p. 181°, which is smoothly converted into the corresponding *anhydride*, $CO_2H\cdot C_6H_3<\begin{matrix}SO_2\cdot NH\\ |\\ CO\text{-}CO\end{matrix}$, colourless crystals, m. p. 261°. Either compound is converted by phenylhydrazine into the *phenylhydrazone*, m. p. 244°. *Ethyl* 2-*sulphonamido*-6-*carbethoxyphenylglyoxylate* has m. p. 107—108° after slight previous softening. The phthalonic acid is smoothly oxidised further to 3-sulphamidophthalic acid, m. p. 165°, which is also readily prepared from 5-sulphonamidotetrahydronaphthalene in two stages. 6-Sulphonamidotetrahydronaphthalene gives a mixture of the possible substituted phthalonic acids, which is smoothly oxidised in acid solution to 4-sulphonamidophthalic acid, m. p. 198—200° (*ethyl* ester, slender needles, decomp. 90° after softening at 80°).

6-Thiol-1 : 2 : 3 : 4-tetrahydronaphthalene (cf. Schroeter, A., 1922, i, 126) is easily transformed into the corresponding *benzoyl* derivative, m. p. 98°, and the *disulphide*, m. p. 66°. It is converted by alkali and methyl iodide into 6-*methylthiol*-1 : 2 : 3 : 4-*tetrahydronaphthal*-

ene, a colourless, almost odourless liquid, b. p. 158—159°/10 mm. *5-Thiol-1 : 2 : 3 : 4-tetrahydronaphthalene*, b. p. 141—143°/11 mm., is prepared from tetrahydronaphthalene-5-sulphonyl chloride; it is transformed by methyl sulphate or methyl iodide into *5-methylthiol-1 : 2 : 3 : 4-tetrahydronaphthalene*, b. p. 158—160°/12 mm. Oxidation of the 6-methylthiol in alkaline solution gives a mixture of ketonic acids which can scarcely be caused to crystallise; if, however, the oxidation is continued in acid solution, *4-methylsulphonylphthalic acid*, m. p. 191° (decomp.), is readily obtained. The acid passes when heated into the corresponding *anhydride*, m. p. 183—184°, from which the *imide*, m. p. 263° (the *potassium* salt is described), is prepared by the action of ammonia at 200—210°. *Ethyl 4-methylsulphonylphthalate* has b. p. about 250°/11 mm. If the anhydride is treated with benzene and aluminium chloride at 80°, it is transformed into the acid, $SOMe_2{\cdot}C_6H_3Bz{\cdot}CO_2H$, m. p. about 230°, which is converted by sulphuric acid containing 5% of anhydride at 100° into 2-methylsulphonylanthraquinone (cf. Gattermann, A., 1912, i, 998). 5-Methylthioltetrahydronaphthalene is converted by oxidation in alkaline solution into *2-methylsulphonyl-6-carboxyphenylglyoxylic acid*, colourless, crystalline granules, decomp. 250°, which is conveniently purified through its *barium* salt, lustrous leaflets ($+3H_2O$). *Ethyl 2-methylsulphonyl-6-carbethoxyphenylglyoxylate* is a very viscous liquid, b. p. 230°/12 mm. The oxidation of the phthalonic acid in acid solution proceeds with unexpected slowness and leads to the production of *3-methylsulphonylphthalic acid*, m. p. 187° (decomp.) in only moderate yield. The new acid is easily transformed into the *anhydride*, b. p. 240°/11 mm., m. p. 182—183°, and thence into the *imide*, colourless leaflets, m. p. 264—266° (the *potassium* salt is described).

H. W.

Simplification of the Gattermann Synthesis of Hydroxyaldehydes. R. Adams and I. Levine (*J. Amer. Chem. Soc.*, 1923, **45**, 2373—2377).—The use of anhydrous hydrogen cyanide in the Gattermann synthesis of hydroxy-aldehydes is avoided by using zinc cyanide instead, in the proportion of 1·5 mols. for 1 mol. of phenol. Somewhat more ether is also recommended, about 150 or 200 c.c. to every 20 g. of phenol; the quantity of coloured by-products is thus reduced. The dry ether may be replaced by dry chloroform, but in this solvent a more highly coloured product is obtained. Using dry ether, and passing in anhydrous hydrogen chloride rapidly for one and a half hours, and then more slowly for thirty minutes, the following yields of hydroxy-aldehyde are obtained from the phenols mentioned: resorcinol, 95%; orcinol, 85%; β-naphthol, 85%; α-naphthol, 72%; pyrogallol, 45%. The imide hydrochloride which actually separates is decomposed by boiling with water or dilute alcohol. Anhydrous zinc cyanide for this reaction is produced by treating aqueous sodium cyanide with magnesium chloride to precipitate any carbonate or hydroxide present, filtering, and adding alcoholic zinc chloride to the filtrate. Since, when zinc cyanide is used, zinc chloride is formed during

the reaction, the addition of the latter reagent is rendered in all cases unnecessary. W. S. N.

The Influence of Substitution in the Components of Binary Solution Equilibria. XLIII. The Binary Systems of *m*-Hydroxybenzaldehyde with Phenols and Nitro-compounds. R. KREMANN and K. POGANTSCH (*Monatsh.*, 1923, **44**, 163—174).—No indications of combination are shown by the freezing-point curves of *m*-hydroxybenzaldehyde and phenol, the two naphthols, the three dihydroxybenzenes, and pyrogallol; the meta-compound thus differs from *p*-hydroxybenzaldehyde, and resembles *m*-nitrobenzaldehyde. The introduction of one nitro-group into the phenol does not affect the nature of the curves with *m*-hydroxybenzaldehyde, but with 2 : 4-dinitrophenol and picric acid the curves become horizontal over considerable distances, indicating formation of highly dissociated compounds, due to the increased total affinity between the two components; the three dinitrobenzenes, 2 : 4-dinitrotoluene, and trinitrotoluene give simple eutectic curves, as do benzoic and salicylic acids. S. I. L.

Catalytic Reduction of Aldehyde Acetals. T. KARIYONE and Y. KIMURA (*J. Pharm. Soc. Japan*, 1923, No. **500**, 746—753).—When benzaldehyde diethyl acetal is reduced in glacial acetic acid solution with hydrogen in the presence of palladised barium sulphate, toluene is easily produced in almost quantitative yield: $C_6H_5{\cdot}CH(OEt)_2+2H_2=C_6H_5Me+2EtOH$. In the same way, *p*-methoxybenzaldehyde and *p*-tolualdehyde diethyl acetals gave *p*-methoxycresol and *p*-xylene, respectively. The *p*-tolualdehyde diethyl acetal is a colourless liquid, b. p. 116—119°/12 mm., d^{22} 1·006, and n^{22} 1·47603. The acetals of cinnamaldehyde and *iso*valeraldehyde and acetophenone and triethyl orthobenzoate do not give corresponding hydrocarbons. Furfuraldehyde diethyl acetal seems to be reduced to a tetrahydro-compound. The authors therefore conclude that only when the aldehyde acetal group is attached directly to the benzene nucleus is the ethoxyl group easily reduced to the methyl group. K. K.

Peroxides of Monoximes. II. R. CIUSA and E. PARISI (*Gazzetta*, 1923, **53**, 667—671; cf. A., 1923, i, 579).—Oxidation of benzaldoxime by means of iodine and sodium carbonate yields results similar to those obtained by Bougault and Robin (A., 1919, i, 489), excepting that the two isomeric dibenzenyloxoazoximes, m. p. 135° and 63°, respectively (A., 1923, i, 1018), are formed.

Oxidation of benzaldoxime by means of nitrous anhydride gives: (1) benzoylbenzaldoxime, (2) benzoic acid, (3) a small proportion of a crystalline *compound*, m. p. 158°, (4) diphenylglyoxime peroxide, and (5) benzenylazoxime.

Treatment of *m*-nitrobenzaldoxime with iodine and sodium carbonate results in the formation of: m-*nitrobenzoyl*-m-*nitrobenzaldoxime*, $C_{14}H_8O_6N_2$, which crystallises in small, colourless needles, m. p. 180°, *m*-nitrobenzoic acid, and the nitrogen-free compound, m. p. 124°, previously obtained (A., 1923, i, 579), but not yet identified. T. H. P.

Aromatic Nitrolic Acids. G. Ruggeri (*Gazzetta*, 1923, **53**, 691—698).—Certain arylnitrolic acids may be obtained by treating the aryl aldoximes with nitrogen peroxide (0·5 mol.), which has been used hitherto for the conversion of aldoximes into the corresponding peroxides or the primary dinitro-hydrocarbons. The results obtained by Ponzio (A., 1906, i, 593, 735), Behrend and Tryller (A., 1895, i, 201), and the author indicate that the initial products of the action of nitrogen peroxide on arylaldoximes are always nitrolic acids. Some of the latter are stable, and may be isolated, whereas others are readily oxidised to dinitro-derivatives of hydrocarbons by excess of the reagent, and others again, by elimination of the nitro-group and union of the residues of two molecules, are transformed into peroxides of the aldoximes. For the latter reaction to occur, the nitrolic acids must exhibit the structure of nitrites, $CHAr{:}N{\cdot}O{\cdot}NO_2$, or of *N*-nitro-derivatives, $CHAr{:}N(NO_2){:}O$; the former gives for the peroxides the formula $[CHAr{:}N{\cdot}O{\cdot}]_2$ and the latter the formula $[CHAr{:}N(:O){\cdot}]_2$, which is in accord with the nitronic structure, $CHAr{:}NH{:}O$, proposed by Staudinger and Miescher (A., 1919, i, 584) for the aldoximes and demonstrated experimentally for many of their derivatives. *p*-Chlorophenylmethylnitrolic and *m*-nitrophenylmethylnitrolic acids are stable in the air if pure and resemble phenylmethylnitrolic acid in being transformable into the peroxides of the corresponding dioximes, but differ from it by being capable of benzoylation and of conversion into 1 : 2 : 4-oxadiazoles. The latter are possibly derived, not directly from the nitrolic acids by simultaneous elimination of a molecule of nitric and one of nitrous acid, but from the aldoxime peroxides formed initially from the nitrolic acids:

$$[CHAr{:}N{\cdot}O{\cdot}]_2 - H_2O = O\!<\!\begin{matrix} N{=}C\,Ar \\ | \\ CAr{:}N \end{matrix}.$$

p-*Chlorophenylmethylnitrolic* (p-*chlorobenznitrolic*) *acid*, $C_6H_4Cl{\cdot}C(:NOH){\cdot}NO_2$, obtained by the action of nitrogen peroxide on *p*-chlorobenzaldoxime in anhydrous ethereal solution, crystallises in pale straw-coloured, slender, silky needles, m. p. 78—79° (decomp.), and dissolves with an intense red coloration in solutions of the alkali carbonates or hydroxides, in the latter case without immediate change but with ultimate decolorisation and separation of a mixture of di-*p*-chlorobenzenylazoxime and di-*p*-chlorobenzildioxime. The same two compounds are formed when the nitrolic acid is heated with various organic solvents. The *benzoyl* derivative of *p*-chlorophenylmethylnitrolic acid, $C_6H_4Cl{\cdot}C(:NOAc){\cdot}NO_2$, crystallises in long, lustrous needles, m. p. 115°.

3 : 5-*Di*-p-*chlorophenyl*-1 : 2 : 4-*oxadiazole*, $\begin{matrix} N{:}C(C_6H_4Cl) \\ | \\ O{\cdot}C(C_6H_4Cl) \end{matrix}\!>\!N$, forms long, flattened, lustrous needles, m. p. 180—181°.

Di-p-*chlorobenzildioxime peroxide*, $C_6H_4Cl{\cdot}C_2N_2O_2{\cdot}C_6H_4Cl$, forms long, white laminæ, m. p. 193—194°.

p-*Chlorophenyldinitromethane*, $C_6H_4Cl{\cdot}CH(NO_2)_2$, obtained by the action of nitrogen peroxide on *p*-chlorobenzaldoxime, crystallises in white needles, m. p. 55° (decomp.). Its *potassium* derivative,

$C_6H_4Cl\cdot CK(NO_2)_2$, forms large, orange-yellow prisms and is highly stable in the air but explodes when heated. The *p*-chlorophenyldinitromethane is accompanied by a small proportion of *p*-chlorobenzaldehyde, the *phenylhydrazone* of which, $C_{13}H_{11}N_2Cl$, crystallises in small, straw-yellow needles, m. p. 132°.

m-*Nitrophenylmethylnitrolic* (m-*nitrobenznitrolic*) *acid*, $NO_2\cdot C_6H_4C(:NOH)\cdot NO_2$, separates in pale straw-coloured, flattened needles, m. p. 89° (decomp.), and behaves like *p*-chlorophenylmethylnitrolic acid towards alkali hydroxide solutions. Its solution in sodium carbonate solution gradually yields a mixture of 3 : 5-di-*m*-nitrophenyl-1 : 2 : 4-oxadiazole and di-*m*-nitrobenzildioxime peroxide. Its *benzoyl* derivative, $NO_2\cdot C_6H_4\cdot C(:NOBz)\cdot NO_2$, crystallises in pale yellow prisms, m. p. 145°, and softens a few degrees below its melting point. T. H. P.

Dioximes. XIII. L. Avogadro (*Gazzetta*, 1923, **53**, 698—707; *Atti R. Accad. Sci. Torino*, 1923, **58**, 269—282).—The results obtained with phenylglyoxime (A., 1923, i, 472) rendered it probable that its derivatives substituted in the nucleus, such as *p*-tolylglyoxime, *p*-chloro- and *p*-bromo-phenylglyoximes, etc., are capable of existing in two forms. The author has now prepared these derivatives by various methods and finds that the modifications described by Söderbaum (Beilstein, III, 92, 95) and Collet (A., 1902, i, 625) are actually mixtures of two individual compounds, inter-related in the same way as the two phenylglyoximes. As α-modifications are designated those which give green nickel salts soluble in cold dilute acetic acid, the β-varieties yielding reddish-brown nickel salts insoluble even in hot dilute acetic acid. The β-forms melt at the higher temperatures, are the more stable, and may be obtained from the α-isomerides by fusion or by heating with dilute acetic acid. The nickel salts of the β-forms are derived by replacement of two oximinic hydrogen atoms, one from each of two molecules of the glyoxime, whereas those of the α-forms are not obtainable pure but are probably formed by the substitution of one atom of the metal for the two oximinic hydrogen atoms of a single molecule. Only the β-compounds are able, in aqueous solution, to attack compact nickel and cobalt, forming the corresponding complex salts.

Owing to the isomerisation of the α- into the β-form under the action of acetic anhydride, the two phenylglyoximes yield but one diacetyl derivative, but the *p*-tolyl- or *p*-chlorophenyl-glyoximes give two distinct diacetyl compounds. Further, the α-forms of *p*-tolyl- and *p*-chlorophenyl-glyoximes, like that of phenylglyoxime, cannot be benzoylated on account of the ease with which they undergo anhydridisation into the corresponding furazans, these being capable of isomerisation into the oximes of *p*-toluoyl and *p*-chlorobenzoyl cyanides :

$$NOH:CR\cdot CH:NOH \rightarrow O\begin{matrix}N:CR\\ N:CH\end{matrix} \rightarrow NOH:CR\cdot CN.$$

The same behaviour is probably exhibited by the two *p*-bromophenylglyoximes, but the author has not investigated the derivatives of these.

As regards the nature of the isomerism of the new glyoximes, the action on the latter of nitrogen tetroxide has not yet been studied, but exclusion of geometrical isomerism is demonstrated by the observation that in the β-forms, but not in the α-forms, the two oximino-groups are equivalent.

α-p-*Tolylglyoxime*, $C_6H_4Me{\cdot}C(NOH){\cdot}CH{:}NOH$, crystallises in white prisms, m. p. 170—171°. The *nickel* salt, $C_9H_8O_2N_2Ni$, forms a greenish-yellow precipitate or a brownish-yellow, amorphous powder which remains unmelted at 300°. The *diacetyl* derivative, $C_{13}H_{14}O_4N_2$, crystallises in white prisms, m. p. 115°, and dissolves in 20% sodium hydroxide solution with formation of *p*-tolylfurazan and the oxime of *p*-toluoyl cyanide. Treatment of the glyoxime in sodium hydroxide solution with benzoyl chloride yields the *benzoyl* derivative of p-*toluoyl cyanide oxime*, $C_6H_4Me{\cdot}C(CN){:}NOBz$, which separates in white needles, m. p. 147—148°.

β-p-*Tolylglyoxime* forms pale straw-yellow laminæ, m. p. 192—193°. Its *nickel* salt, $(C_9H_9O_2N_2)_2Ni$, is obtained as a blood-red, crystalline powder which becomes brown, without melting, at 300°; it is readily decomposed by dilute mineral acids but resists the action of hot acetic acid. The *cobaltous* salt forms a coffee-coloured powder. The *diacetyl* derivative crystallises in white needles, m. p. 73—74°, and is dissolved slowly by 20% sodium hydroxide solution with formation of the original glyoxime.

p-*Tolylfurazan*, $O\!<\!\begin{matrix}N{:}C{\cdot}C_6H_4Me\\ N{:}CH\end{matrix}$, crystallises in prisms of characteristic odour, m. p. 52°, is not affected by concentrated sulphuric, hydrochloric, or nitric acid, but is converted by either boiling water or the hydroxides of the alkali metals into

p-*Toluoyl cyanide oxime*, $C_6H_4Me{\cdot}C(CN){:}NOH$, which crystallises in lustrous laminæ, m. p. 117°, and may be prepared also by the action of sodium and amyl nitrite on the nitrile of *p*-tolylacetic acid.

p-*Chloro-oximinoacetophenone*, $C_6H_4Cl{\cdot}CO{\cdot}CH{:}NOH$, obtained by treating *p*-chloroacetophenone with sodium ethoxide and amyl nitrite, crystallises in straw-coloured needles, m. p. 170°.

α-p-*Chlorophenylglyoxime*, $C_6H_4Cl{\cdot}C(NOH){\cdot}CH{:}NOH$, forms white prisms, m. p. 165°, and its *diacetyl* derivative, microscopic laminæ, m. p. 123—124°. The benzoyl derivative of *p*-chloro-oximinophenylacetonitrile has m. p. 117—118°; Zimmermann (A., 1903, i, 92) gave 115—116°.

β-p-*Chlorophenylglyoxime* crystallises in pale straw-yellow needles or prisms, m. p. 188°. Its *nickel* salt, $(C_8H_5O_2N_2Cl)_2Ni$, forms orange-red prisms which begin to turn brown, without melting, at about 305°. Its *diacetyl* derivative crystallises in white prisms, m. p. 128—129° (decomp.), and its *dibenzoyl* compound in lustrous needles, m. p. 159°.

p-*Chlorophenylfurazan*, $O<\begin{matrix}N:C\cdot C_6H_4Cl\\ |\\ N:CH\end{matrix}$, forms white needles, m. p. 103—104°, has a characteristic odour, is not affected by concentrated sulphuric, hydrochloric, or nitric acid, and is converted by alkali hydroxide or by boiling water into oximino-*p*-chlorobenzyl cyanide. T. H. P.

Dioximes. XIV. G. Ponzio and G. Ruggeri (*Gazzetta*, 1923, **53**, 708—713).—According to Behrend and Schmitz (A., 1904, i, 108), the action of sodium carbonate or hydroxide on methylchloroglyoxime yields a dibasic acid which was, however, not obtained pure. The authors find that gradual addition of dilute aqueous sodium carbonate to a dilute ethereal solution of a chloroglyoxime results in the elimination of two molecules of hydrogen chloride from two molecules of the oxime, the residues then giving dioximes of diacylglyoxime peroxides.

The *dioxime* of *diacetylglyoxime peroxide*, $C_2O_2N_2(CMe{:}N\cdot OH)_2$, obtained from methylchloroglyoxime, crystallises in large prisms or white laminæ, m. p. 145°, and forms a *hydrochloride* which separates in white laminæ; its *dibenzoyl* derivative, $C_{20}H_{16}O_6N_4$, forms white needles, m. p. 160°. This dioxime greatly resembles and is possibly identical with the compound obtained by Behrend and Tryller (A., 1895, i, 201) by the action of hydroxylamine hydrochloride on the oil formed by heating at 80—90° the product of the interaction of acetone and nitric acid (cf. Steffens, A., 1900, i, 74).

The *dioxime* of *dibenzoylglyoxime peroxide*, $C_2O_2N_2(CPh{:}N\cdot OH)_2$, prepared from chlorophenylglyoxime (cf. A., 1923, i, 473), crystallises in white needles with straw-yellow reflection, m. p. 156°, and its *dibenzoyl* compound, $C_{30}H_{20}O_6N_4$, in white prisms, m. p. 148°.

Diphenyltetraketone tetra-oxime, $C_6H_5\cdot[C{:}NOH]_4\cdot C_6H_5$, prepared by reducing the preceding dioxime by means of zinc dust and glacial acetic acid, forms a white, microcrystalline powder, turning yellow at about 230°, m. p. 255—256° (decomp.). Its *tetrabenzoyl* derivative, $C_{44}H_{30}O_8N_4$, crystallises in lustrous, white needles, m. p. 257° (decomp.).

According to Claisen and Manasse (A., 1893, i, 464), the action of sodium hydroxide on chloro-oximinoacetophenone yields sodium benzoate, whilst that of sodium carbonate gives an oil which, on protracted heating, passes into solution. It is now found that treatment of chloro-oximinoacetophenone in ethereal solution with aqueous sodium carbonate solution gives a good yield of dibenzoylglyoxime peroxide. T. H. P.

Dioximes. XV. G. Ponzio (*Gazzetta*, 1923, **53**, 713—715).—Isomerisation of the α- into the β-forms of glyoximes may be effected to some extent by simple fusion, but decomposition occurs before the change reaches completion. Contrary to the statement made by Auwers and Meyer (A., 1889, 403), if benzildioxime, m. p. 207°, is heated to its melting point and then immediately cooled, it is

found to have undergone partial conversion into the isomeride with m. p. 237°. Hence, in this case, as in others, the stable form of the glyoxime is that with the highest melting point, and the prefixes α- and β- require to be interchanged. T. H. P.

Action of Phenylcarbylamine on β-Naphthol. M. PASSERINI (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 165—168).—The reaction occurring when phenylcarbylamine and β-naphthol are boiled in alcoholic solution under a reflux condenser differs from any reaction previously observed with the *iso*nitriles (A., 1921, i, 743, 895; 1922, i, 731; 1923, i, 63).

The *dianil* derivative of 2-*hydroxy*-1-*naphthylglyoxal*,

$$OH\cdot C_{10}H_6\cdot C(:NPh)\cdot CH:NPh,$$

thus obtained, forms lustrous, silky, pink needles, m. p. 169—170°. It yields a benzoyl derivative and, when it is boiled with alcoholic potassium hydroxide solution and the liquid subsequently acidified, the lactone, $C_{10}H_6<\begin{matrix}CO\\O\end{matrix}>CO$, is formed. When heated, the lactone loses carbon monoxide and dioxide, giving a neutral compound, $C_{20}H_{12}O_2$ (? 1 : 2-dioxydinaphthylene, $C_{10}H_6{:}O_2{:}C_{10}H_6$), together with a little β-naphthol, whilst, when treated in acetic acid solution with hydrogen peroxide, it loses carbon dioxide and yields 2-hydroxy-1-naphthoic acid; the lactone forms a yellow, crystalline, *phenylhydrazone*, m. p. 224—225°. Free 2-hydroxy-1-naphthylglyoxal has not been obtained but the corresponding *diphenylhydrazone*, which forms yellow crystals, m. p. 240°, is formed when the above dianil derivative is treated when hot with phenylhydrazine.

T. H. P.

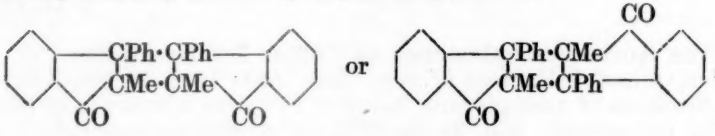
The Aminoacetophenones as Colour Intermediates. G. T. MORGAN and J. E. MOSS (*J. Soc. Chem. Ind.*, 1923, **42**, 461—463T).—Nitration of acetophenone below −11° gives a mixture of 56 to 65% of *m*-nitro- and 31 to 22% of *o*-nitro-acetophenone. At higher temperatures the proportion of the ortho-derivative increases; at 15° there is obtained 35·6% of *o*-nitro-, 32·5% of *m*-nitro-acetophenone, and 20·6% of *m*-nitrobenzoic acid. *o*-Nitroacetophenone is best reduced to *o*-aminoacetophenone with tin and concentrated hydrochloric acid; when dilute acid is used, the product appears to be *o*-acetyl-β-phenylhydroxylamine. *m*-Nitroacetophenone can be reduced quantitatively to the amine by iron filings and water acidified with acetic acid.

With diazo-compounds *m*-aminoacetophenone does not couple to give aminoazo-derivatives, but forms diazoamines. With *p*-nitrodiazobenzene, it gives p-*nitrobenzenediazo*-3-*aminoacetophenone*, pale yellow plates, m. p. 188°. It follows that *m*-aminoacetophenone cannot be used, as can *m*-toluidine, as a middle component for azo dyes; but the aminoacetophenones can be diazotised and used as primary components for such dyes. The dyes obtained from *o*-aminoacetophenone diazotised and coupled with β-naphthol or its sulphonic acids have no definite mordanting properties. This negative result may be taken to support the hydrazone formul-

ation for azo-colours from *o*-aminoacetophenone. *Acetophenone-m-azo-β-naphthol* forms rosettes of glistening, brownish-red, flattened needles with green reflex, m. p. 155°; with concentrated sulphuric acid, it gives an intense, carmine-red coloration, whilst the corresponding dyes from *o*- and *p*-aminoacetophenones give violet and deep purple colorations, respectively. With β-naphthol-6-sulphonic acid, diazotised *o*-, *m*-, and *p*-aminoacetophenones give brick-red to brownish-red dyes, which give, respectively, vermilion, reddish-orange, and carmine colorations with sulphuric acid. They give brick-red shades on wool, the ortho-compound giving the yellowest and the para-compound the darkest shade. E. H. R.

Indones. V. Conversion of 3-Phenyl-2-methylindone into Diphenyldimethyltruxones by the Action of Ultra-violet Rays. REMO DE FAZI (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 227—230).—It has been shown that 3-phenyl-2-methylindone may be obtained from ethyl β-hydroxy-ββ-diphenyl-α-methylpropionate (A., 1916, i, 151), whereas, under similar conditions, ethyl β-hydroxy-ββ-diphenylpropionate yields 3-phenylindone and two isomeric diphenyltruxones (A., 1920, i, 316). When treated with concentrated sulphuric acid, however, 3-phenyl-2-methylindone does not yield a truxone, but gives an emerald-green solution, and when this is poured on to ice the original indone is obtained; consequently diphenyldimethyltruxones cannot be synthesised by this method.

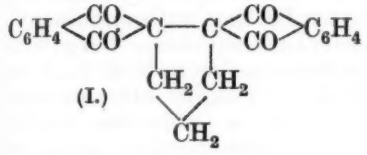
It seems, however, that indones may be transformed into truxones by the action of ultra-violet rays. Under this agency, 3-phenyl-2-methylindone yields a *diphenyldimethyltruxone*,



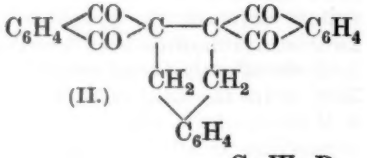
which forms white crystals, m. p. 307—308°, and in benzene solution gradually yields a small proportion of pale yellow crystals, m. p. 259—260°, possibly of another diphenyldimethyltruxone. After repeated crystallisation from alcohol, the compound, m. p. 307—308°, gives with concentrated sulphuric acid an emerald-green solution, which yields the original 3-phenyl-2-methylindone when poured on to ice. T. H. P.

Spirans. XI. Synthesis of Dispirans. D. RADULESCU (*Bull. Soc. Ştiinţe Cluj*, 1922, **1**, 335—336; from *Chem. Zentr.*, 1923, iii, 140; cf. A., 1923, i, 1197, 1211, 1240).—The author has synthesised dispirans from bisdiketohydrindene (Gabriel and Leupold, A., 1898, i, 481) by a method by means of which tri- and penta-spirans also may possibly be obtained. By the action of trimethylene bromide on the dipotassium salt of bisdiketohydrindene in anisole solution at 140°, cyclo*pentanbis*-1 : 2-*diketohydrindene*-1 : 2 : 2 : 2-*dispiran*, $C_{21}H_{14}O_4$ (I) is obtained as light pink, strongly refracting prisms, m. p. 254°; it sublimes above 350°.

1 : 2 : 3 : 4 - *Tetrahydronaphthalenebis* - 1 : 2 - *diketohydrindene* - 2 : 2 : 3 : 2-*dispiran* (II) is obtained by a similar reaction, using *o*-xylylene bromide; it forms pink, strongly refracting prisms with m. p. 265°, subliming above 350°. Bisdiketohydrindene and ethyl bromoacetate yield *ethyl bisdiketohydrindene* - 2 : 2 - *diacetate*, $C_{26}H_{22}O_8$, needles, m. p. 174°.



(I.)



(II.)

G. W. R.

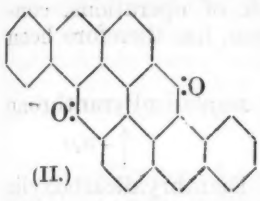
Anthraquinonylurethanes; Anthraquinonylcarbamides. M. Battegay and J. Bernhardt (*Bull. Soc. chim.*, 1923, **33**, [iv], 1510—1536).—A more detailed description of work previously published (A., 1922, i, 1041). The following substances are described. *Anthraquinonyl*-1-*urethane*, yellow spangles, m. p. 215°, prepared by the action of ethyl chloroformate on 1-aminoanthraquinone in nitrobenzene. 4-*Nitroanthraquinonyl*-1-*urethane*, brown crystals, m. p. 245°, from 4-nitro-1-aminoanthraquinone. 4-*Hydroxyanthraquinonyl*-1-*urethane*, red crystals, m. p. 225°, from 1-amino-4-hydroxyanthraquinone, with which ethyl chloroformate appears to react only as regards the amino-group. 4-*Methoxyanthraquinonyl*-1-*urethane*, red needles with a yellow lustre, m. p. 230°, from 1-amino-4-methoxyanthraquinone. 4-*Benzamidoanthraquinonyl*-1-*urethane*, red needles, m. p. 248°, from 4-nitro-1-aminoanthraquinone by benzoylation, reduction with sodium sulphide, and subsequent treatment of the resulting 4-benzamido-1-aminoanthraquinone with ethyl chloroformate. *Anthraquinonyl*-1-*carbamyl chloride*, a yellow solid, decomp. 120°, prepared by the action of dry carbonyl chloride on a nitrobenzene solution of 1-aminoanthraquinone. *Anthraquinonyl*-2-*carbamyl chloride*, a grey solid turning yellow on exposure to air, decomp. 230°, similarly prepared, considerably more stable than its isomeride. 1 : 1′-*Dianthraquinonylcarbamide*, yellow crystals, m. p. 340—350°, by the action of carbonyl chloride on 1-aminoanthraquinone in nitrobenzene in presence of anhydrous sodium acetate, distinguished from the 2 : 2′-isomeride (cf. A., 1911, i, 655) by the production of an orange as distinct from a yellow precipitate on diluting its solution in concentrated sulphuric acid. 1 : 2′-*Dianthraquinonylcarbamide*, a yellow solid, m. p. above 360° with sublimation, prepared by condensing 1-aminoanthraquinone with anthraquinonyl-2-carbamyl chloride in nitrobenzene solution; an attempt to use 2-aminoanthraquinone and anthraquinonyl-1-carbamyl chloride resulted only in the formation of a mixture of α- and β-aminoanthraquinone. 4 : 4′-*Dinitro*-1 : 1′-*dianthraquinonylcarbamide*, dark yellow crystals, m. p. above 360° with sublimation, by the action of carbonyl chloride on 4-nitro-1-aminothraquinone in nitrobenzene in presence of sodium acetate.

4 : 4′ - *Dihydroxy* - 1 : 1′ - *dianthraquinonylcarbamide*, violet - black crystals, m. p. above 360°, from 4-hydroxy-1-aminoanthraquinone. 4 : 4′-*Dimethoxy*-1 : 1′-*dianthraquinonylcarbamide*, a brown, crystalline powder, m. p. above 350°, subliming at 320°, from 4-methoxy-1-aminoanthraquinone. 4 : 4′-*Dibenzamido* - 1 : 1′-*dianthraquinonylcarbamide*, red crystals, m. p. above 350°, from 1-amino-4-benzamidoanthraquinone. 4 - *Nitro* - 1 : 2′ - *dianthraquinonylcarbamide*, yellow crystals, m. p. above 350°, by heating anthranquinonyl-2-carbamyl chloride with 4-nitro-1-aminoanthraquinone. 4-*Hydroxy*-1 : 2′-*dianthraquinonylcarbamide*, reddish-brown crystals, m. p. above 350°, from the acid chloride and 4-hydroxy-1-aminoanthraquinone. 4-*Methoxy* - 1 : 2′-*dianthraquinonylcarbamide*, a yellowish - brown, crystalline powder, m. p. 350°, from the corresponding methoxyl compound. 4-*Benzamido*-1 : 2′-*dianthraquinonylcarbamide*, a reddish-brown solid, m. p. above 350°, from 4-benzamido-1-aminoanthraquinone. *Anthraquinonyl-2-carbamide*, small, yellow crystals, m. p. 360°, by passing dry ammonia into a toluene solution of anthraquinonyl-2-carbamyl chloride; the isomeric acid chloride, treated similarly, yields 1-aminoanthraquinone. *Phenyl-2-anthraquinonylcarbamide*, yellow crystals, m. p. 300°, but decomposition with liberation of aniline starts at 240—250°; prepared by heating aniline with anthraquinonyl - 2 - carbamyl chloride. *Phenylmethyl* - 2 - *anthraquinonylcarbamide*, deep yellow crystals, m. p. 300°, from methylaniline and the acid chloride. p-*Nitrophenyl-2-anthraquinonylcarbamide*, yellow crystals, m. p. 360°, from *p*-nitroaniline. The authors give an account of the behaviour of each of the above substances on solution in concentrated sulphuric acid with subsequent dilution and on solution in aqueous sodium hydroxide together with some indication of the tinctorial possibilities in most cases. H. J. E.

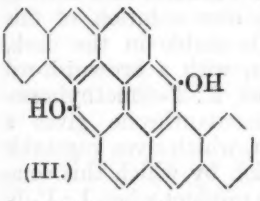
***amphi-iso*Pyranthrone and its Relation to Pyranthrone.** R. Scholl and C. Tänzer (*Annalen*, 1923, **433**, 163—182).—A better yield of 1 : 1′-dianthraquinonyl-2 : 2′-dicarboxylic acid (Scholl, A., 1907, i, 540) is obtained by increasing the quantities of glacial acetic acid and chromic anhydride used in the oxidation of 2 : 2′-dimethyl-1 : 1′-dianthraquinonyl; instead of the latter, pyranthrone may be used. The diketo-acid is reduced by means of zinc dust in boiling, 24% ammoniacal solution in an atmosphere of nitrogen to 1 : 1′-*dianthryl*-2 : 2′-*dicarboxylic acid* (I), pale greenish-yellow needles or rhombohedral leaflets, which chars at about 183°, and melts indefinitely at 273—275° (m. p. 298°, if heated rapidly). It dissolves in cold, concentrated sulphuric acid with a yellowish-green coloration, changing gradually to greyish-black, or, at 70—75°, to dark violet. It gives a *diacid chloride*, compact, brownish-yellow crystals, decomp. 215°, a *diethyl* ester, slender, lemon-yellow needles, sinters 187°, m. p. 201—203° (decomp.), and a *diamide*, thin, colourless needles. When the acid is heated at 275°, or with

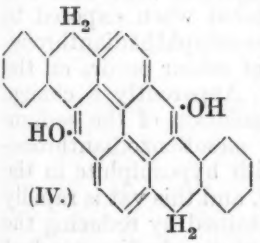
(I.)

zinc chloride at 180—210°, it is partly converted into amphi-iso-*pyranthrone* (II); the condensation is more conveniently effected by heating the acid with phosphoric oxide at 180—190°, or by treating the acid chloride with aluminium chloride in cold nitrobenzene solution. *amphi-iso*Pyranthrone forms slender, lustrous, greyish-violet needles; it does not melt at 360°, but sublimes with partial decomposition at higher temperatures. It dissolves in concentrated sulphuric acid with a reddish-violet coloration, changing to dirty green on the addition of a little water. Its solution in neutral solvents is magenta red.


(II.)

In its chemical behaviour, *amphi-iso*pyranthrone resembles anthraquinone rather than benzoquinone or naphthaquinone. It does not react with aqueous hydriodic acid or aqueous sulphurous acid at 100°, with phenylhydrazine at 200°, or with guaiacum resin or hæmatoxylin in boiling, alcoholic solution. It is even more stable towards stannous chloride and hydrochloric acid than anthanthrone, being only reduced in boiling solution to a hydro-compound, which gives a blue, readily oxidised solution in sodium hydroxide. *amphi-iso*Pyranthrone reacts with alkaline sodium hyposulphite solution at 30—35° to give a blue vat, from which, in contact with air, the original material separates. The blue vat contains amphi*dihydroxypyranthrene* (III), which is isolated as the *di*-p-*bromobenzoate*, lustrous, copper-coloured needles (cf. Scholl, A., 1910, i, 271); it dissolves in boiling, 30% methyl-alcoholic potassium hydroxide, giving a blue solution. If the reduction is effected at 80—90°, a green vat is obtained, which contains amphi-*dihydroxydihydropyranthrene* (IV), which is also isolated as the *di*-p-*bromobenzoate*, a yellow powder. This benzoate is dehydrogenated when boiled with a solvent of high b. p., giving the pyranthrene derivative; with boiling 30% methyl-alcoholic potassium hydroxide it gives, however, a green solution, which gradually turns blue in contact with the air. This change is not observed with the green, aqueous vat itself; *amphi-iso*pyranthrone is gradually precipitated, without the appearance of a blue coloration.


(III.)


(IV.)

*amphi-iso*Pyranthrone is reduced, by heating at 180° with hydriodic acid (b. p. 127°) and red phosphorus, to dihydropyranthrene (Scholl, A., 1910, i, 271). A change in the nomenclature of these compounds is introduced, whereby the system formerly described as "pyranthrene" is now designated "dihydropyranthrene." Dihydropyranthrene is oxidised, by means of chromic anhydride in boiling glacial acetic acid solution, to pyranthrone, or, if an

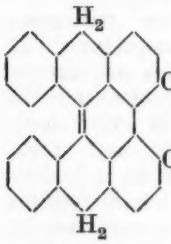
excess of the reagent is used (see above), to 1 : 1′-dianthraquinonyl-2 : 2′-dicarboxylic acid. The following cycle of operations, connecting pyranthrone and *amphi-iso*pyranthrone, has therefore been accomplished:

Pyranthrone $\xleftarrow[\text{oxid.}]{}$ Dihydropyranthrene $\xleftarrow[\text{red.}]{}$ *amphi-iso*Pyranthrone

$\downarrow$ oxid. $\qquad\qquad$ $\uparrow -H_2O$

Dianthraquinonyldicarboxylic acid $\xrightarrow{\text{red.}}$ Dianthryldicarboxylic acid.

At first it seemed possible that the dianthryldicarboxylic acid (I) was really the isomeric acid (V), since 1 : 1-dianthraquinonyl and its derivatives are readily reduced to *meso*benzodianthrone and its derivatives (Scholl and Mansfeld, A., 1910, i, 494). Actually it is found that 2 : 2′-dimethyl-1 : 1′-dianthraquinonyl is converted by the action of copper powder and concentrated sulphuric acid at 40—50° into 2 : 2′-dimethyl*meso*benzodianthrone, yellowish-brown, microscopic prisms, decomp. above 300° (cf. Ullmann and Bincer, A., 1916, i, 483). The blue solution of this compound in concentrated sulphuric acid is stable in the dark, but in sunlight it quickly becomes magenta, with a brownish-red fluorescence, presumably with formation of 2 : 2′-dimethyl*meso*naphthadianthrone. 2 : 2′-Dimethyl*meso*benzodianthrone gives a green vat with alkaline hyposulphite solution, which dyes vegetable fibres yellow. It is probable that the reaction by which this compound is formed is a general one, and that the product when 1 : 1′-dianthraquinonyl-2 : 2′-dicarboxylic acid is used is meso*benzodianthrone*-2 : 2′-*dicarboxylic acid* (V), a dark orange-yellow substance. Its dirty-green solution in concentrated sulphuric acid does not change in the dark, but becomes brownish-red when exposed to light, presumably with formation of *meso*naphthadianthrone-2 : 2′-dicarboxylic acid. The same change of colour occurs on the addition of a little potassium dichromate. Apparently a change to the same acid also takes place when a solution of the sodium salt, but not the ammonium salt, is boiled. *meso*Benzodianthronedicarboxylic acid only gives a green vat with hyposulphite in the presence of cold, very dilute alkali hydroxide, and this vat is rapidly destroyed on warming. A similar vat is obtained by reducing the acid by means of zinc dust and ammonia, but a reduction product cannot be isolated. It is evident that a *meso*naphthadianthrone structure for the acid (I) is to be excluded. W. S. N.



(V.)

The Formation of Borneols from Turpentine Oil. I. Y. Murayama and Keizo Abe (*J. Pharm. Soc. Japan*, 1923, No. 498, 637—644).—American turpentine oil, b. p. 158—161°, d^{15} 0·8644, mainly composed of pinene, was heated with various organic acids at 115—150° during fifteen to twenty hours in a reflux apparatus. Trichloroacetic acid gave a maximum amount of borneol (yield

21%); other acids used were oxalic acid (15%), monochloroacetic acid (14%), phthalic anhydride (3·5%), tartaric acid (0·5%) and citric acid (trace). In the case of oxalic acid, part of the pinene is changed into α-terpinene (nitrosite, m. p. 152°, and nitrolpiperidide, m. p. 153—155°), but not into dipentene. The products from monochloroacetic acid and phthalic anhydride were lævorotatory.

K. K.

The Influence of Substitution in the Components of Binary Solution Equilibria. XLIV. The Binary Equilibria of Fenchone with Phenols. R. KREMANN and K. DIETRICH (*Monatsh.*, 1923, **44**, 175—181).—The freezing-point curve for the system fenchone–α-naphthol shows a maximum at 60·5° for equimolecular proportions; the eutectic of the compound with fenchone lies at 1° and 93% fenchone, with α-naphthol at 55° and 38% fenchone. With β-naphthol an equimolecular compound is indicated by a break at 23°, but the compound only separates with excess of fenchone at the eutectic (10° and 81% fenchone); the m. p. given by Tardy (Beilstein Erg. Bd. 376) corresponds with the complete melting of the solid β-naphthol separated from the compound. The curves for fenchone with phenol, resorcinol, pyrocatechol, pyrogallol, and *o*- and *p*-nitrophenols cannot be completed, as the highly viscous complexes obtained do not crystallise throughout the complete range. With introduction of nitro-groups, the curves may be more nearly completed, picric acid and 2 : 4-dinitrophenol giving complete curves, showing simple eutectics.

S. I. L.

Cathodic Reduction of Ketones, *e.g.*, of Menthone. C. SCHALL and W. KIRST (*Z. Elektrochem.*, 1923, **29**, 537—546).—The authors find that the electrolytic reduction of *l*-menthone in acid solution, employing a cathode of pure lead, mercury, or cadmium, exhibits no depolarisation effect at any stage of the reduction, a result differing from that obtained by Tafel in the case of caffeine and succinimide (A., 1905, ii, 224). As the electrolysis proceeds, the cathode potential increases to a maximum, more slowly in the case of a cadmium cathode than with one of lead or mercury, and then decreases. Employing in the electrolysis a lead cathode prepared as described by Tafel (A., 1900, ii, 588) the authors find that the product of the electrolysis consists principally of *l*-menthol, and the current-efficiency of the process is about 31%. When a roughened bright lead cathode is used, a considerable proportion of menthane results from the reduction, whilst if no diaphragm be employed there is considerable production of pinacol. When a cadmium cathode is employed in the electrolytic reduction of an acid solution of *l*-menthone, the product consists very largely of hexahydrocymene, and the process of reduction is an efficient one. The electrolytic reduction process employing a mercury cathode is described and a process for the production of mercury dimenthyl detailed, likewise an efficient process for the production of menthane, employing a cadmium cathode. Effects observed with platinum and palladium electrodes are briefly referred to. The mechanism

of the reduction process is discussed on the basis of the production of unstable metallic menthyls. J. S. G. T.

The Camphor and Camphenilone Series. L. RUZICKA (*Annalen*, 1923, **434**, 217—218).—A question of priority. Nametkin (A., 1923, i, 934) has overlooked a paper by Ruzicka (A., 1918, i, 398). E. E. T.

The Hydrocarbon $C_{10}H_{16}$ and its Isomerides. A. GAWALOWSKI (*Pharm. Monatsh.*, 1922, **4**, 68—69; from *Chem. Zentr.*, 1923, iii, 846). Oil of turpentine when treated with hydrogen chloride combines, with one or two molecules respectively, according to whether it contains more pinene or camphene, and according to whether a simple or supersaturated product is obtained. Camphene as well as pinene gives additive products with hydrogen chloride. Whilst pinene can give the camphor $C_{10}H_{16}O$ directly with oxygen, this is not possible in the case of camphene. From the compound, $C_{10}H_{17}Cl$, obtained by the action of hydrogen chloride on pinene, a compound, $C_{10}H_{18}O$, may be derived. It yields camphene on dissociation. The compound $C_{10}H_{17}Cl$ is probably bornyl chloride. G. W. R.

The Essential Oil of *Ocimum viride* (Willd.) from Grasse and from New Caledonia: Characterisation of α- and γ-Terpinenes. L. S. GLICHITCH (*Bull. Soc. chim.*, 1923, **33**, [iv], 1536—1539; cf. Goulding and Pelly, P., 1908, 63).—Details are given of the results of examination of two samples of the oil. That from Grasse appears to contain α- and γ-terpinene together with *d*-limonene and possibly some dipentene, whilst that from New Caledonia, although too small in quantity to furnish trustworthy results, contains an unusually small proportion of thymol [cf. *B.*, Jan.]. H. J. E.

The Volatile Oil of Manchurian Peppermint. MANZO NAKAO and CHUZO SHIBUE (*J. Pharm. Soc. Japan*, 1923, No. **499**, 725—738).—Manchurian peppermint, transplanted from Japan, yielded 2·2% of oil, which did not give crystals on being cooled with a mixture of ice and common salt. The constants are as follows: d^{17} 0·914, d^{15} 0·916, acid value 0·535, ester value 139·96, and $[\alpha]_D^{17·5}$ −54·59°. The oil contains 28·65% of free menthol and 39·16% of combined menthol, chiefly as menthyl acetate, but also as (*iso*?)valerate. Menthone and limonene were also detected. The Korean product gave the following constants: d^{15} 0·911, acid value 1·0, ester value 34·92, $[\alpha]_D^{24·5}$ −37·83°; free menthol 58·17%; menthol as menthyl esters 9·73%. K. K.

Substitution and Addition of Chlorine to the Caoutchouc Molecule. J. MCGAVACK (*Ind. Eng. Chem.*, 1923, **15**, 961—962).—When chlorine is passed into a solution of caoutchouc in chloroform, without temperature control, during the first part of the reaction substitution takes place practically to the exclusion of addition. As the reaction proceeds, substitution diminishes and addition increases. In the final product, there are three atoms of substituted chlorine and four atoms of added chlorine, the total

percentage of chlorine being about 65. The apparatus used was provided with flow-meters, by which the flow of ingoing and outgoing gases could be measured; in this way, a continuous record of the progress of the reaction was obtained. E. H. R.

Phytochemistry. I. Betulin. O. DISCHENDORFER (*Monatsh.*, 1923, **44**, 123—140).—Betulin is best obtained from the bark of birch trees of moderate age (15—25 c.c. diameter stem), the bark being removed in spring and summer, when the tissues are softest. After washing, it is extracted by means of alcohol, the crude product purified by crystallisation from dilute alcoholic potassium hydroxide, and obtained by crystallisation from benzene and then from alcohol in snow-white needles, m. p. 251—252°. The yield of crude product is 23% by weight of the bark. The crystals contain one molecule of alcohol, and effloresce in air. Analysis is very difficult, so that the formula is uncertain; Schulze and Pieroh, whose melting-point figure agrees with that now found, suggested $C_{32}H_{52}O_2$ or $C_{33}H_{54}O_2$ (A., 1922, i, 1045), but the mean of several concordant analyses indicates $C_{30}H_{50}O_2$ or $C_{30}H_{52}O_2$. The molecular weight by the micro-method of Rast (A., 1922, ii, 421) was 432, and by the freezing-point method with naphthalene 448 (mean).

Betulin diacetate, m. p. 214° (Schulze and Pieroh give 216—217°), crystallises in rhombic bisphenoids, [$a : b : c = 0{\cdot}99165 : 1 : 0{\cdot}79830$]. *Monobromobetulin diacetate*, $C_{30}H_{49}O_2Br(OAc)_2$, has m. p. 193°. *Betulin dibenzoate*, m. p. 181°, forms monoclinic-prismatic needles, with pseudo-hexagonal habit; [$a : b : c = 1{\cdot}0298 : 1 : 0{\cdot}6458$; $\beta = 82°\ 56'$]; *betulin di-p-bromobenzoate* is obtained as sheaves of needles, m. p. 221—222°.

*allo*Betulin identical with the product obtained by Schulze and Pieroh is also obtained by the action of hydrogen bromide on betulin in chloroform solution; the crystals are triclinic-pedial, [$a : b : c = 0{\cdot}60666 : 1 : 1{\cdot}03745$; $\alpha = 90°\ 11'$, $\beta = 95°\ 6'$, $\gamma = 90°\ 7'$]; the suggestion that this substance is isomeric with betulin is supported, and its acetate and formate are prepared; analyses of all these support the formula $C_{30}H_{50}O_2$ for betulin and allobetulin. S. I. L.

Strophanthin. II. The Oxidation of Strophanthidin. W. A. JACOBS (*J. Biol. Chem.*, 1923, **57**, 553—567; cf. A., 1923, i, 123).—By oxidation of strophanthidin with permanganate in acetone solution an *acid*, $C_{23}H_{30}O_7,\frac{1}{2}H_2O$, stout plates or leaflets, m. p. 185—190° (with effervescence) after sintering above 175°, $[\alpha]_D^{26}$ +54·8° in methyl alcohol, has been obtained. It gives with concentrated sulphuric acid a yellow coloration which rapidly changes through orange to red and purple, and forms a *silver* salt, $C_{23}H_{29}O_7Ag,2H_2O$, small plates and prisms, a *dimethyl* ester, $C_{24}H_{32}O_7,H_2O$, six-sided tablets, m. p. about 160—163° (with frothing) after softening above 150°, $[\alpha]_D^{27}$ +57·6° in methyl alcohol, and a *benzoate*, $C_{31}H_{36}O_8$, minute prisms, m. p. 243—244° (corr.), $[\alpha]_D^{29}$ +61·0° in acetone. The dimethyl ester gives with sulphuric acid a yellow coloration which deepens to orange-red with a purple fluorescence. The acid still contains a lactone group; the product

of hydrolysis, however, is reconverted into the same, and not an isomeric, acid on acidification. When the lactone group of the new acid is hydrolysed with alkali and the reaction product oxidised with permanganate in alkaline solution, the secondary alcohol group which is liberated is oxidised to a carbonyl group with the formation of an *acid*, $C_{23}H_{30}O_8$ (isomeric with strophanthic acid), $[\alpha]_D^{28}$ +28° in pyridine, which crystallises either in the anhydrous form, m. p. 276—278° (effervescence) after sintering, or with two molecules of water of crystallisation, m. p. 268—270° after sintering and darkening, according to the conditions of crystallisation, and gives a yellow colour with sulphuric acid which changes through orange to red with a green fluorescence. It forms a *barium* salt, $C_{23}H_{28}O_8Ba,6H_2O$, silky needles, and a *dimethyl* ester, $C_{25}H_{34}O_8$, platelets and prisms, m. p. 251—252° (effervescence) after sintering at 246°, $[\alpha]_D^{22}$ −12·0° in acetone. The latter yields a *benzoate*, $C_{32}H_{38}O_9$, thin platelets, m. p. 249—251° (decomp.), $[\alpha]_D^{20}$ +7·5° in acetone, a *phenylhydrazone*, $C_{31}H_{40}O_7N_2$, lustrous platelets, m. p. 265—266° (decomp.), and an *oxime*, $C_{25}H_{35}O_8N$, flat needles, m. p. 272—274° (decomp.) after darkening and sintering. Although the acid does not appear to be a lactone, yet when heated with 2% sodium hydroxide the reaction mixture yields, on acidification, a third *acid*, $C_{23}H_{32}O_9,2\frac{1}{2}H_2O$, glistening needles, m. p. 185—187° (effervescence), $[\alpha]_D^{28}$ −37·0° in pyridine, which gives a yellow colour with sulphuric acid, changing to red with a green fluorescence. The analytical figures for this acid, as well as for some of its derivatives, were not entirely satisfactory, but no other formula appears possible. The following derivatives were prepared: *dimethyl* ester, $C_{25}H_{36}O_9$, prisms, m. p. 205—206°, no appreciable rotation; *benzoate* of dimethyl ester, $C_{32}H_{40}O_{10}$, microscopic plates and prisms, m. p. 172—174°; *oxime* of dimethyl ester, $C_{25}H_{37}O_9N,H_2O$, rhombic prisms, m. p. 158—160° (frothing) after preliminary sintering.

An improved method for the preparation of strophanthic acid is described and the following revised constants are given: m. p. about 270° (effervescence), $[\alpha]_D^{26}$ −22·0° in methyl alcohol. With sulphuric acid, it gives a yellow colour changing through orange to red. Contrary to the statement of Feist, strophanthic acid is a lactone; after hydrolysis with alkali, the original acid may be recovered almost quantitatively by acidification, thus differing from strophanthidin, which, under these conditions, yields *iso*strophanthidin. This suggests that strophanthic acid is an oxidation product of the latter substance. Strophanthic acid does not contain a carbonyl group but still retains an alcoholic hydroxyl group as shown by the formation of a *benzoate* of the dimethyl ester, $C_{32}H_{38}O_9$, glistening prisms, m. p. 233—235°, $[\alpha]_D^{20}$ −7·0° in acetone. The dimethyl ester of strophanthic acid melts at 251—253°, and not at 214° as stated by Windaus and Hermanns (A., 1915, i, 704). The view of the latter authors, that strophanthic acid is formed from strophanthidin by oxidation of a methyl group, appears to be untenable; it is concluded from the above results that the attack takes place at the carbonyl group both in the formation of this acid and of the acid $C_{23}H_{30}O_7$ described above. E. S.

Strophanthin. III. Crystalline Kombe Strophanthin. W. A. JACOBS (*J. Biol. Chem.*, 1923, **57**, 569—572; cf. preceding abstract).—The author considers that strophanthin has one of the following formulæ: $C_{32}H_{48}O_{12}$ or $C_{31}H_{46}O_{11}$. It crystallises with $3H_2O$ and contains one methoxyl group. The sugar will accordingly have the formula $C_9H_{18}O_7$ or $C_8H_{16}O_6$ and probably contains the methoxyl group. Attempts to isolate it in a crystalline form have been unsuccessful. From the fact, however, that strophanthin gives with acetic acid, ferrous sulphate, and a few drops of sulphuric acid a deep purple colour which changes through blue to green on the addition of water (a colour reaction which resembles that given by digitoxin and cymarose), it appears probable that the sugar is a deoxy-compound of the same type as these substances. E. S.

Action of Xanthydrol on Semicarbazide, Substituted Semicarbazides, Semicarbazones, and Benzoylhydrazine. A. DOUCET (*Compt. rend.*, 1923, **177**, 1120—1123).—In presence of not more than one molecular proportion of xanthydrol, semicarbazide affords a monoxanthyl derivative (already known); in presence of not less than 2 mols. of xanthydrol, a *dixanthyl* derivative (m. p. 184—185°) results. To determine the constitution of these products, the interaction of xanthydrol and substituted semicarbazides, semicarbazones, and benzoylhydrazine has been studied. Xanthydrol and benzaldehyde semicarbazone give a *monoxanthyl* derivative (m. p. 227—228°), also obtainable from monoxanthylsemicarbazide and benzaldehyde. Xanthydrol and acetone semicarbazone give a *monoxanthyl* derivative (m. p. 213—214°), also obtained by the interaction of acetone and monoxanthylsemicarbazide. Hence, monoxanthylsemicarbazide must have the formula:

$$NH_2\cdot NH\cdot CO\cdot NH\cdot CH<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>O.$$

Again, benzoylhydrazine with xanthydrol gives a *monoxanthyl* derivative (m. p. 178—179°); phenylsemicarbazide,

$$NHPh\cdot CO\cdot NH\cdot NH_2,$$

gives a *monoxanthyl* derivative (m. p. 210—211°); whilst diphenylsemicarbazide, $NPh_2\cdot CO\cdot NH\cdot NH_2$, also gives a *monoxanthyl* derivative (m. p. 153—154°). Hence the above dixanthylsemicarbazide (m. p. 184—185°) must have the formula:

$$O<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>CH\cdot NH\cdot NH\cdot CO\cdot NH\cdot CH<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>O.$$

Phenylsemicarbazide, $NHPh\cdot NH\cdot CO\cdot NH_2$, gave a *monoxanthyl* derivative (m. p. 160—161°) and a *dixanthyl* derivative (m. p. 184—185°), whereas with diphenylsemicarbazide,

$$NHPh\cdot NH\cdot CO\cdot NHPh,$$

only a *monoxanthyl* derivative (m. p. 171—172°) was obtained.

E. E. T.

Aryl-1 : 3-benzodioxans (Arylmethylenesaligenins). R. ADAMS, A. W. SLOAN, and B. S. TAYLOR (*J. Amer. Chem. Soc.*, 1923, **45**, 2417—2420).—It is shown that the reaction between

saligenin and benzaldehyde to give 2-phenyl-1 : 3-benzodioxan (Adams, Fogler, and Kreger, A., 1922, i, 660) is a general one. Derivatives of the reagents mentioned usually react at 100° within from five to thirty minutes, although sometimes nearly two hours may be required. The addition of benzoic acid is seldom necessary. Cinnamaldehyde, but not formaldehyde, acetaldehyde, or butaldehyde, also undergoes condensation. Definite products are not obtained from nitrosaligenin.

The 2-*aryl*-1 : 3-*benzodioxans*, $C_6H_4<\begin{matrix}CH_2\cdot O\\ O-CHR'\end{matrix}$, derived from saligenin and *p*-chlorobenzaldehyde, *p*-bromobenzaldehyde, or *m*-nitrobenzaldehyde have m. p., respectively, 107—107·5°, 117—117·5°, and 88—89·5°. Bromosaligenin, $C_6H_3Br^{(5)}\cdot OH^{(2)}\cdot CH_2\cdot OH^{(1)}$, condenses with the following aldehydes to give the corresponding *bromobenzodioxans*, the m. p. of which are quoted: benzaldehyde, m. p. 85°, *p*-chlorobenzaldehyde, m. p. 147—148°, *p*-bromobenzaldehyde, m. p. 143—144°, cinnamaldehyde, m. p. 118—120°. Methylsaligenin, $C_6H_3Me^{(5)}\cdot OH^{(2)}\cdot CH_2\cdot OH^{(1)}$, is satisfactorily prepared by the reduction of *p*-methylsalicylaldehyde in alcoholic solution by means of hydrogen, platinum oxide, and ferrous chloride (cf. Carothers and Adams, A., 1923, ii, 310). It is condensed with benzaldehyde, and with *p*-bromobenzaldehyde, to give *methylbenzodioxans* having m. p., respectively, 90° and 130°. W. S. N.

Derivatives of Thiodiglycol, Diethylene Disulphide, and Thioxan. E. Fromm and B. Ungar (*Ber.*, 1923, **56**, [*B*], 2286—2289).—Thiodiglycol [ββ-dihydroxyethyl sulphide] is converted when distilled with potassium hydrogen sulphate into water, 1 : 4-thioxan, $O<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>S$ (cf. Clarke, T., 1912, **101**, 1788), and diethylene disulphide, $S<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>S$. The latter compound is oxidised by hydrogen peroxide (two equivalents) in glacial acetic acid solution to *diethylenedisulphoxide*, $OS<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>SO$; by three equivalents to *diethylenesulphoxidesulphone*, $OS<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>SO_2$, m. p. 278—279°, and by four equivalents to the *disulphone*, m. p. above 300°. The sulphoxide-sulphone is converted by boiling, concentrated hydriodic acid into *diethylenesulphonesulphide*, m. p. 200°.

Thioxan, b. p. 147°, is converted by iodine in hot glacial acetic acid solutio inton the corresponding *di-iodide*, $O<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>SI_2$, m. p. 66—67°, and by bromine in the presence of anhydrous ether into the *dibromide*, m. p. 75—80° (decomp.); with boiling ethyl iodide, it gives the *sulphonium iodide*, $O(CH_2\cdot CH_2)_2S\cdot EtI$, slender, yellow crystals, m. p. 85°. Oxidation of thioxan with regulated amounts of hydrogen peroxide gives successively the corresponding *oxide*, $O<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>SO$, colourless plates, which is too hygroscopic to permit analysis, and the *sulphone*, $C_4H_8O_3S$, long, colourless

needles, m. p. 130°. Boiling concentrated hydriodic acid transforms the compound last mentioned into ββ′-*di-iodoethylsulphone*, colourless needles, m. p. 203°, which is converted by benzylmercaptan and sodium hydroxide into *dibenzylthioldiethylsulphone*,

$$SO_2(CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2Ph)_2,$$

colourless, lustrous leaflets, m. p. 100°; hydrogen peroxide oxidises the latter substance to the *trisulphone*, $SO_2(CH_2{\cdot}CH_2{\cdot}SO_2{\cdot}CH_2Ph)_2$, large leaflets, m. p. above 300°. H. W.

The Anhalonium Alkaloids. VI. Anhalonine and Lophophorine. E. Späth and J. Gangl (*Monatsh.*, 1923, **44**, 103—114). —Contrary to the statement of Heffter (A., 1896, i, 267), the relation between these two alkaloids isolated from *Anhalonium Lewinii* is the simplest possible, lophophorine being now found to be identical with *N*-methylanhalonine. The quaternary methyl iodide compound, which is lævorotatory, has m. p. 223°, then changing into the racemic form of m. p. 242—243°. Only about 1 g. of each substance was available, but the Weber-Tollens reaction having indicated the presence of a methylenedioxy-group, the constitutions were elucidated by syntheses of the two alternatives, viz., for anhalonine (*a*) 8-methoxy-6 : 7-methylenedioxy-1-methyltetrahydro*iso*quinoline, and (*b*) 6-methoxy-7 : 8-methylenedioxy-1-methyltetrahydro*iso*quinoline, lophophorine being the corresponding *N*-methyl compound. The *N*-methyl derivative of the compound of constitution (*a*) was synthesised by the action of magnesium methyl iodide on cotarnine iodide, yielding α-methyldihydrocotarnine, corresponding with formula (*a*). The second synthesis was carried out from myristicine by ozonisation to the aldehyde, condensation of this with nitromethane and reduction to homomyristicylamine, the acetyl compound of which condenses to a dihydro*iso*quinoline compound in presence of phosphoric oxide; reduction finally gave the compound (*b*) required, the quaternary iodide of which was found to be identical with the racemic form of lophophorine methyl iodide.

Attempts were made to resolve the racemic synthetic anhalonine into the optically active forms by means of tartaric acid and of bromocamphorsulphonic acid, but were unsuccessful. The presence of the optically active alkaloids anhalonine and lophophorine with the inactive anhalonidine and pellotine in the same plant is probably due to the mobility of the asymmetric carbon atoms in the latter.

The following compounds are described: the *picrate* of the quaternary base from lophophorine, $C_{20}H_{22}O_{10}N_4$, m. p. 211—212°; the *picrate* of 8-methoxy-6 : 7-dioxymethylene-1 : 2-dimethyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline, m. p. 176—177°; the *methiodide* of α-methyldihydrocotarnine, m. p. 225°; *ω-nitro-3-methoxy-4 : 5-methylenedioxystyrene*, $C_{10}H_9O_5N$, prepared from myristicine aldehyde by condensation with nitromethane, yellow needles, m. p. 212—213°; *N-acetylhomomyristicylamine*, m. p. 130°; *6-methoxy-7 : 8-dioxymethylene-1-methyldihydroisoquinoline*, m. p. 60—62°, and its *picrate*, m. p. 206—208°; the *hydrochloride* of (synthetic) racemic

anhalonine, and the *trinitro*-m-*cresolate* of the quaternary base from lophophorine, $C_{21}H_4O_{10}N_4$, m. p. 171—172°. S. I. L.

The Action of Penetrating Radium Rays on Caffeine. A. KAILAN (*Annalen*, 1923, **433**, 272—277).—When a 1·2% aqueous solution of caffeine was exposed in the dark at 6—11° for sixty-two days to the radiation from 110·4 mg. of radium chloride, it became alkaline to the extent of 0·0018*N* and the specific conductivity was increased by 170×10^{-6} reciprocal ohms; there was therefore a gain in equivalent conductivity of 95 reciprocal ohms. The substance to the formation of which this phenomenon is due is volatile at 150°, and is, most probably, ammonium or methylammonium formate. It is shown that the sum of the ammonia and methylamine molecules produced per second, and the number of ion pairs absorbed per second, are in the ratio 2 : 3, whilst the ratio of caffeine molecules decomposed to the number of ion pairs absorbed is most probably 1 : 3, the extreme possible figures being 2 : 3 and 1 : 6. The decomposition of caffeine by means of penetrating radium rays therefore accords with the general rule, that the number of molecules destroyed is of the same order as the number of ion pairs from the total absorbed radiation (cf. Kailan, A., 1922, ii, 467). Although Leipen has shown (A., 1889, 1017) that the action of ozone on caffeine in aqueous suspension leads to the reaction $C_8H_{10}O_2N_4+3O+2H_2O=C_5H_6O_3N_2+2CO_2+NH_2Me+NH_3$, the formation of parabanic acid could not be detected. Moreover, a similar reaction involving hydrogen peroxide is improbable, since insufficient of the latter is formed to account for the quantity of caffeine decomposed (Kailan, *loc. cit.*). It is considered more likely that the action of the radium rays, or of the ions deirved from them, is direct, or that, perhaps, activated oxygen plays a part in the reaction. W. S. N.

Synthesis of Natural Cocaine. R. WILLSTÄTTER, O. WOLFES, and H. MÄDER (*Annalen*, 1923, **434**, 111—139).—The methyl and ethyl esters of tropinonecarboxylic acid have now been obtained in large quantities. The *methyl* ester, m. p. 111°, obtained (using sodium and cymene) from methyl 1-methylpyrrolidinediacetate (Willstätter and Bommer, A., 1921, i, 122), forms a *hydrate*, $C_{10}H_{15}O_3N,2·5H_2O$, m. p. 100° (not sharp), a *monohydrochloride*, prisms, m. p. 180°, and a *benzoyl* derivative, needles, m. p. 75—76°, which has no marked anæsthetic action, and resists hydrogenation. Ethyl tropinonecarboxylate, b. p. 107°/0·5 mm., or 170°/25 mm., forms a *hydrate*, $C_{11}H_{17}O_3N,2H_2O$, m. p. 63—65°, a *picrate*, m. p. 135—136°, a *methiodide*, m. p. 190—192°, and a *hydrochloride*, m. p. 168°.

Methyl acetonedicarboxylate, with potassium hydroxide and methyl alcohol, affords the dipotassium derivative, which condenses with succindialdehyde and methylamine to give a 65% yield of methyl tropinonecarboxylate (the mother-liquors, after treatment with boiling sulphuric acid, affording a little tropinone).

On repeating the reduction of the last-named ester, followed by hydrolysis of the ψ-ecgonine methyl ester (m. p. 128°) (Willstätter and Bode, A., 1903, i, 361), a *hydrate* of the previously described

r-ψ-ecgonine was obtained; and also (in addition to ψ-ecgonine methyl ester), *r*-ecgonine methyl ester. The latter, when heated successively with hot potassium hydroxide and methyl alcohol containing hydrogen chloride, was converted into the *r*-ψ-ester.

The resolution of *r*-ψ-cocaine (benzoyl *r*-ψ-ecgonine methyl ester, m. p. 81·5°) has again been attempted, using *d*-tartaric, malic, *d*-camphor-, *d*-α-bromocamphor-β-, and *d*-α-bromocamphor-π-sulphonic acids. In all cases, however, partial racemates were obtained; the base at the same time was found to possess the simple formula, $C_{17}H_{21}O_4N$. The following salts of *r*-ψ-cocaine are described: *hydrogen* d-*tartrate*, m. p. 164°, $[M]_D^{20}$ +39°; d-*α-bromocamphor-β-sulphonate*, m. p. 182—183°, $[M]_D^{20}$ +312°; d-*camphorsulphonate*, m. p. 218°, $[\alpha]_D^{20}$ +9·19°. For comparison, the corresponding salts of *d*-ψ-cocaine were prepared: *hydrogen*-d-*tartrate*, m. p. 139°, $[M]_D^{20}$ +191°; d-α-*bromocamphor*-β-*sulphonate*, m. p. 206—207°, $[M]_D^{20}$ +446°; d-*camphorsulphonate*, m. p. 222°, $[\alpha]_{20}^{D}$ +37·31°.

When, however, the *salt* of *r*-ψ-ecgonine methyl ester with *d*-α-bromocamphor-β-sulphonic acid was crystallised from ethyl acetate–alcohol mixtures, the d-*base*–d-*acid* salt separated as prisms, m. p. 201°, $[\alpha]_D^{20}$ +71·42—72·6°; the mother-liquors yielding the l-*base*–d-*acid* salt, m. p. 115°. Decomposition of the former salt gave d-*ψ-ecgonine methyl* ester, m. p. 116°, $[\alpha]_D^{20}$ +19·5° (*hydrochloride*, $[\alpha]_D^{20}$ +23·68°). With *d*-α-bromocamphor-π-sulphonic acid, *r*-ψ-ecgonine methyl ester gave a less soluble l-*base*–d-*acid* salt, m. p. 243°, $[\alpha]_D^{20}$ +43·47°.

d-ψ-Ecgonine methyl ester gives the same *methiodide* (m. p. 209°) as is obtained from methyl iodide and the (cold) *l*-ester. The latter, with warm methyl iodide, however, gives the methiodide (m. p. 165°) described by Einhorn and Friedlaender (A., 1893, i, 537) as that of the *d*-ester. *r*-ψ-Ecgonine methyl ester or *r*-ecgonine methyl ester give the methiodide (m. p. 185°) already described by Willstätter and Bode (*loc. cit.*). The true *l*- and *dl*-ecgonine methyl ester *methiodides* (m. p., respectively, 164° and 162°) are formed (together with the *hydriodides*) by treating the corresponding esters with methyl iodide in presence of a solvent. The methiodides of the ψ-series are more stable towards alkali than their isomerides of the other series.

r-Ecgonine methyl ester, on benzoylation, gave *r*-cocaine (m. p. 79—80°) (*hydrochloride*, m. p. 187°). Of the various salts of the base obtained by precipitation methods, only the *permanganate* was obtained crystalline, the *nitrate*, *hydriodides*, and *mercuri-iodides* separating as oils.

The resolution of *r*-cocaine was effected through the *hydrogen* d-*tartrate*, the salt of the *l*-base separating as the *dihydrate*, prisms, m. p. 114—115°. Using *l*-tartaric acid, *d*-cocaine hydrogen-*l*-tartrate was the less soluble salt. The identity of the active alkaloids was established crystallographically.

The product described by Willstätter and Bode (*loc. cit.*) as ψ-tropine-*O*-carboxylic acid is now shown to be *r*-ecgonine (as trihydrate). *dl*-Cocaine or *dl*-ecgonine methyl ester, on hydrolysis with

cold barium hydroxide, affords the same compound, which melts first at 93—118°, becoming solid and remelting, with decomposition, at 203° (slow heating) or 212° (rapid heating). The hemi-hydrochloride, $(C_9H_{15}O_3N)_2,HCl$, has m. p. 247° (decomp.) and the chloroaurate, m. p. 205° (one preparation having m. p. 175°, as recorded previously).

From the reduction product of tropinonecarboxylic ester, a third *r-ecgonine* was isolated as the *dihydrate*, prisms, m. p. 110° and 229° (with frothing). The *hydrochloride*, $C_9H_{15}O_3N,HCl,H_2O$, is sparingly soluble, and has m. p. 230—233°. Boiling concentrated hydrochloric acid converts the new ecgonine into *r*-anhydroecgonine, identical with the product of the action of hydrogen chloride (in glacial acetic acid) on *dl*-ecgonine or on *dl*-ψ-ecgonine. The anhydro-compound crystallises with $1H_2O$ and has m. p. 226—230° (decomp.), the *methiodide* of its methyl ester melting at 180°.

[With R. GOTTLIEB.]—The ψ-configuration favours anæsthetic action, the most powerful anæsthetic being *d*-ψ-cocaine. The racemate of the ψ-series is more powerful than *l*-ψ-cocaine or than *dl*-cocaine, whilst, in both series, the *d*-form, when injected subcutaneously, acts less powerfully than the *l*-forms on the central nervous system.

Crystal measurements [H. STEINMETZ and F. MÜLLBAUER] are given as follows:

d-ψ-Ecgonine methyl ester-*d*-α-bromocamphor-β-sulphonate (rhombic, $a:b:c=0{\cdot}6338:1:0{\cdot}3429$); *l*-$\psi$-ecgonine methyl ester-*d*-α-bromocamphor-π-sulphonate (rhombic $a:b:c=0{\cdot}3598:1:0{\cdot}6692$); *r*-cocaine (rhombic, $a:b:c=0{\cdot}6192:1:0{\cdot}6223$; *d*- and *l*-cocaine (synthetic and natural) (monoclinic, $a:b:c=0{\cdot}8551:1:1{\cdot}0248$; $\beta=106°\ 56'$); and the new *r*-ecgonine dihydrate (triclinic, $a:b:c=1{\cdot}2494:1:\ldots$; $\alpha=58°\ 50'$, $\beta=122°\ 7'$, $\gamma=113°\ 2'$).

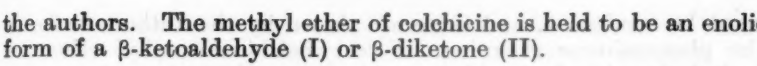
E. E. T.

Action of the Grignard Reagent on Cocaine. Tropyldimethyl Carbinol. S. FRÄNKEL and G. GRUBER (*Annalen*, 1923, **433**, 241—246).—The action of an excess of magnesium methyl iodide on cocaine in ice-cold ethereal solution gives phenyldimethyl carbinol (*benzenesulphonate*, rhombic leaflets or large, pointed columns, m. p. 51·5°), and *tropyldimethylcarbinol*; the latter yields the syrupy *oxalate* and *tartrate*, hygroscopic *hydrochloride*, colourless needles, m. p. 162°, *dibenzoate*, clusters of needles, m. p. 90°, yellow *di*-p-*nitrobenzoate*, m. p. 103° (*hydrochloride*, m. p. 185°), and *di*-p-*aminobenzoate*, a powder, m. p. 178°. Colour reactions are given for the dibenzoate, the di-*p*-nitrobenzoate, and the di-*p*-aminobenzoate. The free carbinol, the dibenzoate, and the dinitrobenzoate have an anæsthetic action, the former being the more powerful. The diaminobenzoate has no anæsthetic action, but, like the free base, it has a bitter taste.

W. S. N.

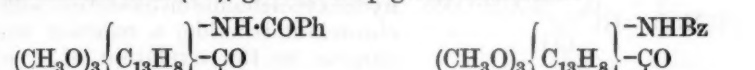
Constitution of Colchicine. A. WINDAUS and H. SCHIELE (*Nachr. K. Ges. Wiss. Göttingen*, 1923, 17—36; from *Chem. Zentr.*, 1923, iii, 673—675; cf. Windaus, A., 1911, i, 904—906; 1915, i, 708—709).—The constitution of colchicine is discussed by

the authors. The methyl ether of colchicine is held to be an enolic form of a β-ketoaldehyde (I) or β-diketone (II).



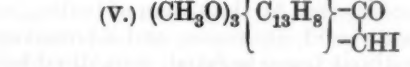
(I.) (II.)

Colchiceine gives the characteristic colour reaction for aldo- and keto-enols with ferric chloride. The ready hydrolysis of colchicine to colchiceine also suggests the enolic structure. The dibenzoyl derivative (III) of trimethylcolchicinic acid (obtained by removal of one molecule of acetic acid from colchiceine) gives no reaction with ferric chloride, whilst its hydrolytic product, *N*-benzoyltrimethylcolchicinic acid (IV), gives a deep green coloration.



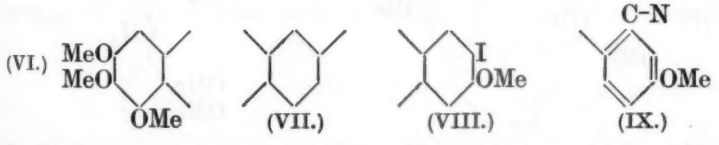
(III.) (IV.)

The behaviour of colchiceine with bromine and acetic acid, and also with iodine and potassium hydroxide suggests the keto-aldehyde formula (I). In the first case, tribromocolchiceinic acid, $C_{21}H_{20}O_7NBr_3$, is obtained. This contains a carbonyl group which can occur only through oxidation of an aldehyde group. *N*-Acetyliodocolchinol (V) obtained in the latter case is to be considered as an iodophenol. Colchiceine is therefore closely related to the aromatic *o*-hydroxyaldehydes.



(V.)

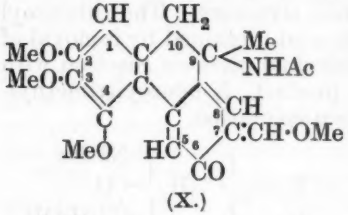
The authors demonstrate the existence of three six-atom carbon rings in colchicine. Colchicine, colchiceine, trimethylcolchicinic acid, and *N*-acetyliodocolchinol all give, on oxidation with potassium permanganate, 3 : 4 : 5-trimethoxy-1 : 2-phthalic acid, suggesting the grouping (VI). Fusion with potassium hydroxide followed by oxidation gives terephthalic acid and trimellitic acid, which suggests the presence of a partly hydrogenated benzene ring of grouping (VII).



(VI.) (VII.) (VIII.) (IX.)

A third ring is demonstrated by the oxidation of *N*-acetyliodocolchinol methyl ether, $C_{21}H_{24}O_5NI$, with nitric acid and potassium permanganate. Amongst the products a compound is formed, which by reduction gives 4-methoxyphthalic acid; this the authors suppose to be 5-iodo-4-methoxybenzene-1 : 2-dicarboxylic acid arising from a ring (VIII). Oxidation of *N*-acetylcolchinol methyl ether gives 4-methoxy-*o*-phthalic acid from the third carbon ring, which suggests the grouping (IX). The three carbon rings

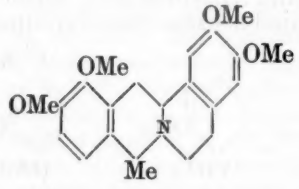
must be condensed, and these are shown by the authors to be in the phenanthrene grouping. *N*-acetylcolchinol methyl ether by hydrolysis with hydrochloric acid gives colchinol methyl ether hydrochloride, which contains four methoxyl groups and one amino-group. This can be degraded by the Hoffmann reaction into a quaternary ammonium hydroxide, $C_{22}H_{31}O_4N$, which on being heated in a vacuum loses water and trimethylamine, giving 2 : 3 : 4 : 6-*tetramethoxy*-9-*methylphenanthrene*, hexagonal tablets, m. p. 111°. The latter by hydrolysis with hydriodic acid and subsequent reduction yields 9-*methylphenanthrene*, $C_{15}H_{12}$, m. p. 88°. Since colchicine, $C_{22}H_{25}O_6N$, gives hydroxycolchicine on oxidation with chromium trioxide, a reaction analogous to the oxidation of α-tetrahydronaphthalene, a reactive methylene group must be present. It is concluded that the constitution of colchicine is represented by the formula (X).



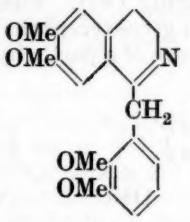
(X.)

G. W. R.

The Constitution of Corydaline. E. Späth and E. Mosettig (*Annalen*, 1923, **433**, 138—154).—A *compound*, colourless crystals, m. p. 111—112°, having the formula (I), has been synthesised by the following method. *o*-Vanillin methyl ether, hippuric acid, fused sodium acetate, and acetic anhydride are heated at 100°, giving an *azlactone*, $C_{18}H_{15}O_4N$, glistening, yellow needles, m. p. 167—168°, which is converted by the action of boiling, aqueous alkali hydroxide into benzoic acid, ammonia, and *o*-homoveratroylformic acid; the latter, without being isolated, is oxidised by means of hydrogen peroxide, giving *homo-o-veratric acid* (3 : 4-*dimethoxyphenylacetic acid*), m. p. 82—83°. The acid is now heated at 175—180° with homoveratrylamine; or its chloride, prepared by the action of phosphorus pentachloride, is treated in ethereal



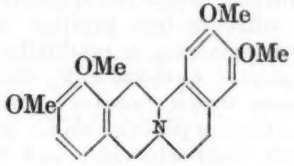
(I.)

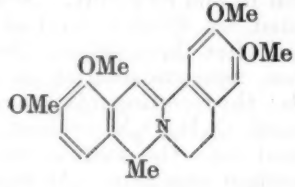


(II.)

solution with homoveratrylamine, and the solution shaken with dilute, aqueous alkali hydroxide solution. Either procedure gives the *amide*, $C_6H_3(OMe)_2\cdot NH\cdot CO\cdot CH_2\cdot C_6H_3(OMe)_2$, m. p. 130—130·5°. The action of phosphoric oxide on a boiling, toluene solution of the amide causes ring formation, with production of the *dihydroisoquinoline* derivative (II), (*picrate*, m. p. 172—174°), which is reduced by the action of tin on its boiling, aqueous-alcoholic hydrochloric acid solution to the similarly constituted, colourless, amorphous

tetrahydroisoquinoline derivative (m-*nitrobenzoyl* derivative, yellow crystals, m. p. 148—149°). This compound gives resinous products when condensed with acetaldehyde diethylacetal, but can be condensed with methylal, by the action of boiling hydrochloric acid, to give the *base* (III), m. p. 158—159° (*hydrochloride*), which, being a compound of the tetrahydroberberine type, is dehydrogenated by heating at 100° with ethyl-alcoholic iodine. The *quaternary iodide* of the resulting *dihydro-base* is not fully purified, but is treated with a boiling ethereal solution of magnesium methyl iodide. The *methyldihydro-base* (IV), which is isolated from the

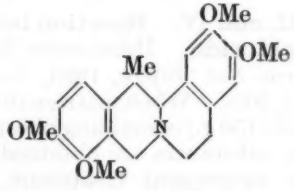
(III.) 

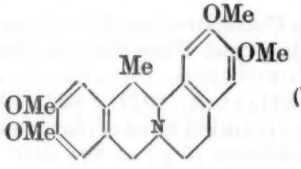
 (IV.)

product, is difficult to purify owing to the ease with which it undergoes oxidation; the crude product has m. p. 100—110°. The final stage in the synthesis of the compound (I) is the reduction of the base (IV) by means of platinised zinc and hot, dilute sulphuric acid.

The formula (I) was at one time advanced by Gadamer, and by Haars (A., 1905, i, 462) as a possible one for corydaline. The compound having this structure is, however, quite different from either of the inactive corydalines. Consequently, the formulæ (V) and (VI), the former of which (cf. Späth and Lang, A., 1922, i, 168) has been accepted by Gadamer and Bruchhausen (A., 1922, i, 675), are the most probable for corydaline. It is possible, however, that it has a structure similar to that of bulbocapnine, which contains a phenanthrene ring, and in which the nitrogen atom is monocyclically bound and carries a methyl group. In order to decide whether the nitrogen atom in corydaline takes part in one ring or in two, degradation has been carried out by the methods of Hofmann and of Emde.

Corydaline methiodide is too insoluble to be decomposed by means of sodium hydroxide at 100°; it is therefore treated in

(V.) 

 (VI.)

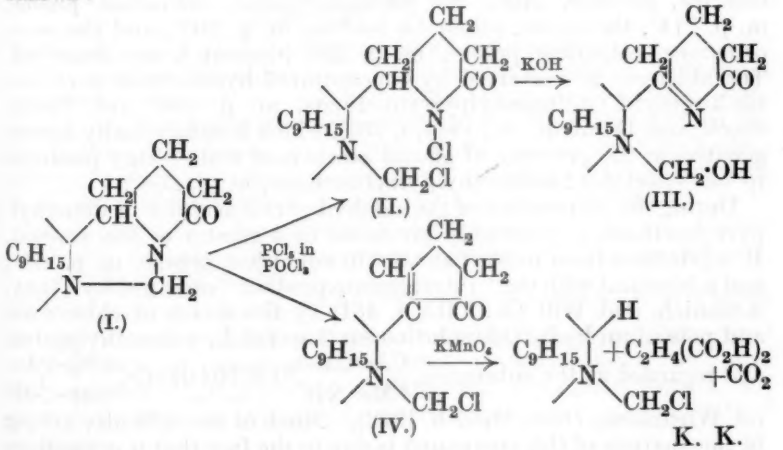
aqueous-alcoholic solution with silver nitrate, and, after removal of the silver iodide, the corydaline methonitrate solution is boiled with potassium hydroxide. The resulting crude methylcorydaline (Freund and Josephi, A., 1894, i, 100) is not purified, but is converted successively into the methiodide and the methochloride;

the latter is then boiled in aqueous solution with sodium hydroxide. The products are a nitrogen-free substance, trimethylamine, and traces of ammonia. The presence of dimethylamine could have been detected with certainty, since its condensation product with *m*-nitrobenzoyl chloride, m-*nitrodimethylbenzamide*, m. p. 84—85°, can readily be isolated from an aqueous solution containing 8% of trimethylamine hydrochloride and 0·77% of dimethylamine hydrochloride. Evidently the complete elimination of nitrogen from corydaline by Hofmann's method occurs in two, and not three, stages. This indicates, to some extent, that the nitrogen is bound in one ring only. Nevertheless, when the degradation is conducted by Emde's method, a nitrogen-free product is only obtained after three stages. Sodium amalgam is gradually added to a hot, aqueous solution of *corydaline methochloride*, colourless crystals; the resulting mixture of bases, which contains a crystalline compound, $C_{23}H_{29}O_4N$, evidently methylcorydaline (*ibid.*), is again converted into the methiodide, and methochloride, and treated with sodium amalgam. At this stage a hydrocarbon is not produced, and an almost quantitative yield of tertiary amine is obtained. The latter is again subjected to the same treatment, with the formation of trimethylamine and an unsaturated *hydrocarbon*, m. p. 87—88°, which passes, on catalytic hydrogenation, to an amorphous product.

The constitution of corydaline is therefore similar to that of berberine, and not to that of bulbocapnine. This agrees with the results of Herzig and Meyer (A., 1898, i, 53), who could not detect the presence of a methylimide group in corydaline by their method; their observations have been, in general, confirmed. It is probable that during the degradation by Hofmann's method, the corydaline alkylhalide (nitrate) partly decomposes into its original constituents, whilst simultaneously a strongly basic product is formed, containing monocyclically bound nitrogen. This could then form a quaternary salt, and undergo a further step in the degradation. Thus two stages will be accomplished in apparently one operation, and the production of a hydrocarbon, which really takes place in three steps, will appear only to require two. The use of the Hofmann degradation may therefore lead to misleading results, when applied to questions of alkaloid constitution. W. S. N.

The Constitution of Matrine. III. and IV. Reaction between Matrine and Phosphorus Pentachloride. Heisaburo Kondo and Tokusaburo Sanada (*J. Pharm. Soc. Japan*, 1923, No. 498, 644—659; cf. A., 1921, i, 882; 1922, i, 269).—When matrine (formula I) (5 g.) is added to phosphoryl chloride (50 g.) containing phosphorus pentachloride (5 g.) at 80—100°, two substances are obtained, their amount differing according to the subsequent treatment. One, matrine monochloride (IV), $(C_{15}H_{22}ONCl)_n$, slightly yellowish, boat-like crystals, m. p. 240—242° (decomp.), is an unstable compound insoluble in almost all organic solvents. On treatment with dilute, acidified potassium permanganate solution it gives succinic acid and a base, $C_{10}H_{18}NCl$; the latter corresponds with a volatile

base, $C_{10}H_{19}N$, obtained by the dry distillation of a mixture of matrine and zinc dust (A., 1921, i, 882). The chloroplatinate, yellow, rhombic prisms, m. p. 309° (decomp.), has not the formula $(C_{15}H_{22}NCl)_2,H_2PtCl_6$, but $(C_{10}H_{18}NCl)_2,H_2PtCl_6$. The monochloride gives also a chloroaurate, a yellow, amorphous substance, m. p. 180° (decomp.), mercurichloride, m. p. 287° (decomp.), picrate, and dichromate. The other substance, matrine dichloride (II), $C_{15}H_{24}ON_2Cl_2$, light yellow, long, rhombic plates, m. p. 146°, is stable towards heat and potassium permanganate solution; [*chloroplatinate*, crystalline powder, m. p. 234° (decomp.); *chloroaurate*, crystalline powder, m. p. 224—225° (decomp.)]. By treatment with 0·2*N*-alcoholic potash in the cold, the dichloride gave a compound (III), $C_{15}H_{24}O_2N_2,HCl$, one-third of which yielded matrine, and two-thirds an amorphous compound on reduction with glacial acetic acid and 3% sodium amalgam; the amorphous substance was converted into cinnamic acid and an amorphous base by oxidation with potassium permanganate solution. When the saponification is conducted at 100°, an amorphous *base*, $C_{14}H_{25}ON$ (*chloroaurate*, m. p. 148°; *mercurichloride*, m. p. 182°), and a potassium salt of an imino-acid, $C_{15}H_{25}O_3N_2K$, m. p. 205°, are produced. By reducing with glacial acetic acid and sodium amalgam or tin and hydrochloric acid, the dichloride is easily converted into matrine. From these results, the authors conclude that matrine is a saturated base not containing a double bond between carbon and nitrogen atoms, and that the chlorination causes the opening of a ring, one of the chlorine atoms becoming attached to the nitrogen atom which formed a lactam with the carbonyl group, and the other to the methylene group adjoining the nitrogen. The changes may be shown as follows:



K. K.

Spermine. I. The Base Isolated from Cholera Cultures by Kunz. F. WREDE and E. BANIK (*Z. physiol. Chem.*, 1923, **131**, 29—37).—A base, supposed to be identical with spermine from human sperm, was isolated by Kunz (A., 1888, 1122), who attributed

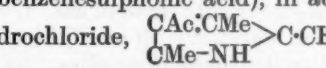
to it the formula C_2H_5N. It has again been investigated. It forms a chloroplatinate, $C_5H_{14}N_2,H_2PtCl_6$, rhombs and needles, a phenylcarbimide, $C_{19}H_{24}O_2N_4$, fine, white needles, m. p. 210°, and is identical with cadaverine [pentamethylenediamine]. W. O. K.

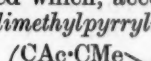
Spermine. II. The Base Isolated by Schreiner from Sperm. F. WREDE and E. BANIK (*Z. physiol. Chem.*, 1923, **131**, 38—53).—A reinvestigation has been made of the base spermine, which Schreiner claimed to have isolated (A., 1879, 72). A base has been obtained in very small yield, forming a chloroaurate, containing C=7·78%, H=2·61%, N=4·03%, Au=47·40, 47·60, 48·41%, agreeing with the formula $C_5H_{18}O_2N_2,H_2Au_2Cl_8$, dense nodular, crystalline masses, m. p. 216—218° (decomp.). No phenylcarbimide could be isolated, and therefore it is not piperazine, which forms a *phenylcarbimide*, fine crystals, m. p. 305—310°, with sublimation, besides a *chloroaurate*, which does not melt at 275°. The trade article "Sperminum-Poehl" appears on analysis to consist of an inorganic phosphate, along with some organic contamination containing nitrogen. W. O. K.

Some Transformations of 3-Acetyl-2 : 4-dimethylpyrrole. Tripyrrylmethanes. I. HANS FISCHER and H. AMMANN (*Ber.*, 1923, **56**, [*B*], 2319—2331).—3-Acetyl-5-aldehydo-2 : 4-dimethylpyrrole, $\begin{matrix}CAc{=}{=}CMe\\ |\quad\quad\ |\\ CMe{:}C(CHO)\end{matrix}>NH$, colourless needles, m. p. 166°, is prepared in a maximal yield of 64·6% when a slow current of dry hydrogen chloride is passed into a suspension of 3-acetyl-2 : 4-dimethylpyrrole and hydrocyanic acid in anhydrous ether and the product is decomposed with cold water. The corresponding *aldazine*, decomp. 299°, the *phenylhydrazone*, colourless prisms, m. p. 214°, the *oxime*, colourless leaflets, m. p. 203°, and the *semicarbazone*, colourless prisms, m. p. 236 (decomp.), are described. The aldehyde is converted by concentrated hydrochloric acid into bis-3-acetyl-2 : 4-dimethylpyrrylmethene, m. p. 200° (cf. Piloty, Stock, and Dormann, A., 1914, i, 755), which is catalytically hydrogenated in the presence of glacial acetic acid and spongy platinum to bis-3-acetyl-2 : 4-dimethylpyrrylmethane, m. p. 268°.

During the preparation of the aldehyde, tri-3-acetyl-2 : 4-dimethylpyrrylmethane is invariably produced in a greater or less amount. It crystallises from methyl alcohol in colourless prisms, m. p. 270°, and is identical with the "intermediate product" obtained by Piloty, Krannich, and Will (A., 1915, i, 461) by the action of chloroform and potassium hydroxide solution on 3-acetyl-2 : 4-dimethylpyrrole and regarded as the substance, $\begin{matrix}CAc{\cdot}CMe\\ ||\quad\quad\\ CMe{-}NH\end{matrix}>C{\cdot}CH(OH){\cdot}C<\begin{matrix}CMe{\cdot}CAc\\ |\quad\quad||\\ NH{-}C{\cdot}Me\end{matrix}$ (cf. Wiedmann, *Diss.*, Munich, 1922). Much of the difficulty arising in the analysis of this compound is due to the fact that it crystallises from ethyl alcohol with half a molecule of solvent, from which it can be completely freed only with great difficulty. It separates from methyl alcohol or glacial acetic acid in the *forms*,

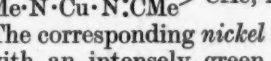
$$C_{25}H_{31}O_5N_5,\tfrac{1}{2}MeOH,$$

m. p. 270°, and $C_{25}H_{31}O_5N_5 \cdot C_2H_4O_2$, m. p. 187° (decomp.), respectively. All attempts to establish the presence in it of a hydroxyl group by means of the chlorides of phosphorus or hydrogen chloride were unsuccessful and led to the production of Piloty's methene hydrochloride. The constitution of the substance is placed beyond doubt by its synthesis from 3-acetyl-5-aldehydo-2 : 4-dimethylpyrrole and 3-acetyl-2 : 4-dimethylpyrrole under the influence of alcoholic potassium hydroxide, whereby it is found that the best yields are obtained when one molecular proportion of the aldehyde is treated with two molecular proportions of the pyrrole. It is further shown that the hydrolysis of Piloty's "intermediate product" by concentrated hydrochloric acid gives 3-acetyl-2 : 4-dimethylpyrrole (which is identified by the well-crystallised azo-dye produced with diazobenzenesulphonic acid), in addition to Piloty's dipyrrylmethene hydrochloride, 
The formation of the tripyrrylmethane compound in Piloty's experiments is readily explained, but its production by means of hydrocyanic acid is more difficult to interpret. It is tentatively ascribed to incomplete reaction of the acid, and combination of the aldehyde formed on addition of water with unchanged pyrrole. The course of the reaction appears, however, to be considerably influenced by slight changes in the experimental conditions. If the product of the action of hydrogen chloride and hydrocyanic acid on 3-acetyl-5-aldehydo-2 : 4-dimethylpyrrole is treated with well-cooled ammonia, a compound, colourless quadratic prisms, decomp. 167—168°, is obtained which, according to its analysis, is regarded as *bis*-3-*acetyl*-2 : 4-*dimethylpyrrylmethylamine*,



the investigation of the substance is not yet complete.

The action of chloroform and methyl-alcoholic potassium hydroxide solution on ethyl 2 : 4-dimethylpyrrole-3-carboxylate gives *tri*-3-*carbethoxy*-2 : 4-*dimethylpyrrylmethane*, $C_{28}H_{37}O_6N_3$, short, colourless prisms, m. p. 194°, which is converted by hydrochloric acid into bis-3-carbethoxy-2 : 4-dimethylpyrrylmethene, m. p. 213°, and ethyl 2 : 4-dimethylpyrrole-3-carboxylate.

Bis-3-acetyl-2 : 4-dimethylpyrrylmethene dissolved in boiling alcohol is converted by Schweizer's reagent into the copper salt, 
CAc, reddish-brown prisms with a green reflex. The corresponding *nickel* salt, $C_{34}H_{38}O_4N_4Ni$, red, hexagonal leaflets with an intensely green reflex, decomp. about 290°, and the *zinc* salt, $C_{34}H_{38}O_4N_4Zn$, cinnabar-red, hexagonal leaflets, are described; the zinc salt exhibits a green fluorescence when dissolved in alcohol.

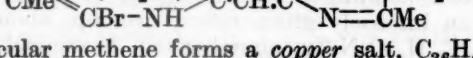
3-Acetyl-5-aldehydo-2 : 4-dimethylpyrrole is converted by the action of sodium ethoxide and hydrazine hydrate at 180° into a *substance*, colourless, volatile needles, m. p. 66°, which has not been investigated completely. Under similar conditions, 3-acetyl-

2 : 4-dimethylpyrrole is converted into cryptopyrrole in good yield, whereas 3-acetyl-2 : 4 : 5-trimethylpyrrole loses its acetyl residue and becomes transformed into 2 : 4 : 5-trimethylpyrrole. A liquid is isolated as by-product of the latter change, the picrate of which has m. p. 137°; its identity has not yet been established. H. W.

Action of Bromine on Substituted Pyrroles and Syntheses of α-Brominated Dipyrrylmethene Dyes. HANS FISCHER and H. SCHEYER (*Annalen*, 1923, **434**, 237—251; Fischer, *Sitzungsber. Akad. München*, 1915, 401).—Ethyl 2 : 4-dimethylpyrrole-3 : 5-dicarboxylate combines with bromine (1 mol.) to give a red, unstable *additive* compound (m. p. 120°, with gas evolution), which separates into its components on crystallisation or on keeping. Excess (4 mols.) of bromine converts the ester into *ethyl 4-methyl-2-bromomethylpyrrole-3 : 5-dicarboxylate* (colourless needles, m. p. 155—156°), which (1), when warmed with methyl (or ethyl) alcohol, gives the corresponding 2-*methoxymethyl* (or *ethoxymethyl*) derivative, m. p. 79° (72°); (2) on reduction with hydrogen and platinum black is converted into the original 2 : 4-dimethyl ester; (3) with boiling water gives a *substance*, $C_{24}H_{32}O_9N_2$ (colourless needles, m. p. 113—114°); and (4) with zinc dust and glacial acetic acid affords a *substance*, $C_{13}H_{17}O_5N$ (needles, m. p. 120°).

Ethyl 3-acetyl-2 : 4-dimethylpyrrole-5-carboxylate with 1 mol. of bromine gives a well-defined but unstable *additive* compound, and with 4 mols. of bromine gives ethyl 3-bromo-4-methyl-2-bromomethylpyrrole-5-carboxylate (Fischer, A., 1922, i, 758). This substance, on warming with methyl (or ethyl) alcohol, affords the corresponding 2-*methoxymethyl* (*ethoxymethyl*) derivative, m. p. 98—99° (101°), and, on warming with water, gives a mixture of substances.

Di- and tri-substituted pyrroles, with no substituent in position 2, when treated with an excess of bromine, afford crystalline dyes (cf. Fischer, *loc. cit.*), which are now shown to be (for the greater part), dipyrrylmethenes, giving well-defined zinc and copper salts, the latter being very similar to the copper salts of mesobilirubinogen. The mechanism of the formation of the dipyrrylmethenes is probably as follows (to take the case of the dye from ethyl 2 : 4-dimethylpyrrole-3-carboxylate): the 5-hydrogen atom in this compound reacts with the bromomethyl group in the first-formed ethyl 5-bromo-4-methyl-2-bromomethylpyrrole-3-carboxylate to give hydrogen bromide and a dipyrrylmethane, which then, in presence of excess of bromine, is oxidised to the methene,



This particular methene forms a *copper* salt, $C_{36}H_{40}O_8N_4Br_2Cu$, red rhombohedra with a green reflex (decomposing at 194—196°), and a *zinc* salt, $C_{36}H_{40}O_8N_4Br_2Zn$, red prisms with a golden reflex, m. p. 242°.

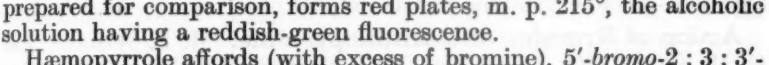
Ethyl 4-methyl-2-bromomethylpyrrole-3 : 5-dicarboxylate and ethyl 3-bromo-4-methyl-2-bromomethylpyrrole-5-carboxylate, when oxidised in presence of trisubstituted pyrroles, afford methene dyes. 2 : 4-Dimethylpyrrole with an excess of bromine affords 3 : 3′ : 5′-

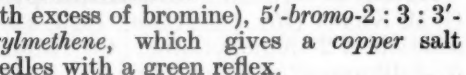
tribromo-2 : 4 : 4′-*trimethyldipyrrylmethene hydrobromide*, red needles, darkening at 210° and not melting at 260°. The free *base* forms red needles with a blue reflex, m. p. (if heated rapidly) 192° (with charring). *Copper* salt, $C_{24}H_{20}N_4Br_6Cu$, needles (red by transmitted and green by reflected light) decomposing at 211°. *Zinc* salt (red by transmitted and golden-yellow by reflected light) has a reddish-green fluorescence in alcoholic solution.

The *zinc* salt of bis-2 : 4-dimethyl-3-carbethoxypyrrylmethene, prepared for comparison, forms red plates, m. p. 215°, the alcoholic solution having a reddish-green fluorescence.

Hæmopyrrole affords (with excess of bromine), 5′-*bromo*-2 : 3 : 3′-*trimethyl*-4 : 4′-*diethyldipyrrylmethene*, which gives a *copper* salt (m. p. 158° [indef.]), red needles with a green reflex.

3-Acetyl-2 : 4-dimethylpyrrole behaves somewhat peculiarly with excess of bromine. The well-defined *dye* obtained ($C_{14}H_{14}ON_2Br_4$) probably has one of the following formulæ :





5-Bromo-3-acetyl-2 : 4-dimethylpyrrole, when treated with bromine, gives the red *compound*, $C_{14}H_{15}ON_2Br_5$, the latter affording a *zinc* salt, red needles with a golden reflex.

Chloroform solutions of the above copper and zinc salts and also of the copper salt of bis-2 : 4-dimethylpyrrylmethene (A., 1923, i, 707) have been examined spectroscopically. E. E. T.

Complex Salts. G. Spacu and R. Ripan (*Bul. Soc. Ştiinţe Cluj*, 1922, **1**, 542—566; from *Chem. Zentr.*, 1923, iii, 601—602; cf. A., 1923, i, 832).—The authors have prepared a series of salts which show all variations between true complex salts and unstable compounds which are considered to be double salts. The dissociation of such double salts into their components is conditioned by the solvent. In non-dissociating solvents they behave as complex salts. The following complex or double salts are described : Double *salt* of the composition $[Mg(SO_4)_2],[Ni(H_4O_2)_6],2H_2O$, formed by allowing a saturated equimolecular aqueous solution of magnesium sulphate and nickel sulphate to evaporate at 25°; green crystals, losing water on keeping in air; *tetrapyridine nickel magnesium sulphate*, $[MgSO_4)_2],[Ni(C_5H_5N)_4]$, formed by warming and finally boiling magnesium nickel sulphate with pyridine; a green, crystalline powder which slowly loses pyridine in air; *monoaquopentapyridine nickel zinc sulphate*, $[Zn(SO_4)_2],[Ni(C_5H_5N)_5,H_2O]$, prepared from zinc nickel sulphate and pyridine, a green, crystalline powder, fairly stable in air. Double *salt*, $[Mg(SO_4)_3],[Co(H_2O)_6]_2,9H_2O$, prepared by allowing a saturated equimolecular solution of magnesium sulphate and cobalt sulphate to evaporate; a pink, crystalline powder; complex *salt*, $[Mg(SO_4)_3],[Co(C_5H_5N)_2(H_2O)_4]_2$, pink, crystalline powder which rapidly loses pyridine with decolorisation; *pentabenzylamineaquocobalthexa-aquocobaltmagnesium sulphate*, $[Mg(SO_4)_3][Co(C_7H_9N)_5,H_2O][Co(H_2O)_6]$, a violet, crystalline powder; *hexapyridinecobaltmonopyridinepenta-aquocobaltcopper sulphate*,

$[Cu(SO_4)_3][Co(C_5H_5N)_6][Co(C_5H_5N)(H_2O)_5]$, a violet powder losing pyridine on keeping in air; complex *salt*, $[CuCl_6][Co(C_5H_5N,HCl)_3]_2$, obtained by the action of a strong ethyl-alcoholic solution of hydrogen chloride on the preceding compound; a green, crystalline powder, stable in air; complex *salt*, $[CuBr_6][Co(C_5H_5N,HCl)_3]_2,H_2O$, similarly prepared, dark violet crystals; complex *salt*,

$$[CoBr_6][Cu(C_5H_5N,HCl)_3]_2,$$

crystals, stable in air; complex *salt*, $[Cu(SO_4)_2][Co(C_7H_9N)_3(H_2O)_3]_2$, a greyish-green, crystalline powder, stable in air. G. W. R.

Action of Bromine on 2-Aminopyridine. J. P. Wibaut and G. M. Kraay (*Rec. trav. chim.*, 1923, **42**, 1084—1091).—An aqueous solution of 2-aminopyridine, at 0°, absorbs bromine vapour to give 3 : 5-dibromo-2-aminopyridine, m. p. 104·1—104·5°, identical with the product obtained indirectly from 3 : 5-dibromo-1-methyl-2-pyridone by Fischer and Chur (A., 1916, i, 741), who found, for the latter compound, the m. p. 180° (Wibaut and Kraay give 179·5—180·5°, Decker and Kaufmann [A., 1911, i, 1023] giving 176°). The dibromoaminopyridine, prepared by either method, gives an acetyl derivative, m. p. 160—161°, a benzoyl derivative, m. p. 181—182°, and a picrate, m. p. 232—232·4°. Fischer and Chur, for the last three substances, obtained the respective m. p. 102°, 142—143°, and 228°. E. E. T.

The Course of the Reduction of Pyridinecarboxylic Acids to Nitrogen-free Products. O. Mumm and K. Brodersen (*Ber.*, 1923, **56**, [*B*], 2295—2301).—It has been established that in the remarkable reduction of pyridinecarboxylic acids to nitrogen-free products the group ·CH:N·CH: is converted into the complex ·CO·O·CH_2·. It appears probable that the primary product is a dihydrocyclic derivative, which is converted by the sodium hydroxide derived from the sodium amalgam into an open-chain dialdehyde. In view of their unstable nature, there is, however, little probability of the isolation of such compounds. The authors have therefore directed their attention to derivatives containing substituents in the 2- and 6-positions which should give rise to the more stable ketones, and have selected the readily accessible 6-phenyl-2-methyl-pyridine-3 : 4-dicarboxylic acid (cf. Mumm and Böhme, A., 1921, i, 439). Under suitable conditions, the acid is transformed into β-benzoyl-α-acetylmethylsuccinic acid whilst, in addition, the isolation of very unstable, unsaturated nitrogenous products has been achieved. The course of the change may therefore be represented by the scheme :

$$\begin{array}{l} \mathrm{CPh{\cdot}CH{:}C{\cdot}CO_2H} \\ \mathrm{N{-}CMe{:}C{\cdot}CO_2H} \end{array} \xrightarrow{+2H} \begin{array}{l} \mathrm{CPh{:}CH{-}CH{\cdot}CO_2H} \\ \mathrm{NH{\cdot}CMe{:}C{\cdot}CO_2H} \end{array} \xrightarrow{\text{NaOH}} \begin{array}{l} \mathrm{COPh{\cdot}CH_2{\cdot}CH{\cdot}CO_2H} \\ \mathrm{H_2N{\cdot}CMe{:}C{\cdot}CO_2H} \end{array}$$

or

$$\begin{array}{l} \mathrm{NH_2{\cdot}CPh{:}CH{\cdot}CH{\cdot}CO_2H} \\ \mathrm{COMe{\cdot}CH{\cdot}CO_2H} \end{array} \xrightarrow{\text{NaOH}} \begin{array}{l} \mathrm{CH_2Bz{\cdot}CH{\cdot}CO_2H} \\ \mathrm{COMe{\cdot}CH{\cdot}CO_2H} \end{array}$$

The reduction of an alkaline solution of 6-phenyl-2-methyl-pyridine-3 : 4-dicarboxylic acid by sodium amalgam (2 atomic proportions) leads to the formation of *β-benzoyl-α-acetonylpropionic acid*, $CH_2Bz{\cdot}CH(\cdot CH_2{\cdot}CO{\cdot}Me){\cdot}CO_2H$, long, flattened rhombohedra, m. p. 83°, and after resolidification, 135° (*phenylhydrazone*, m. p.

204°), which is readily converted into the corresponding *lactone*, m. p. 135°, found to be identical with the synthetic product (cf. Miethke, *Dissert.*, Kiel, 1922). With four atomic proportions of sodium, 6-phenyl-2-methylpyridine-3 : 4-dicarboxylic acid gives *γ-phenyl-α-acetonyl-γ-butyrolactone*, $\begin{matrix}\mathrm{CHPh{\cdot}CH_2}\\ \mathrm{O\text{———}CO}\end{matrix}\!>\!\mathrm{CH{\cdot}CH_2{\cdot}COMe}$, or *α-benzoylmethyl-γ-valerolactone*, $\begin{matrix}\mathrm{CHMe{\cdot}CH_2}\\ \mathrm{O\text{———}CO}\end{matrix}\!>\!\mathrm{CH{\cdot}CH_2Bz}$, a very viscous, almost colourless liquid, b. p. 198—220°/0·5—0·6 mm., whereas with six atomic proportions of the metal *αβ′-hydroxypropyl-γ-phenyl-γ-butyrolactone*, $\begin{matrix}\mathrm{CHPh{\cdot}CH_2}\\ \mathrm{O\text{———}CO}\end{matrix}\!>\!\mathrm{CH{\cdot}CH_2{\cdot}CHMe{\cdot}OH}$ (which could not be satisfactorily purified), is produced. The *barium* salt, $(C_{13}H_{17}O_4)_2Ba$, and the *silver* salt, m. p. 185° (decomp.), of the corresponding acid are described. The lactone is isomerised by alcoholic hydrogen chloride into *αβ′-hydroxy-β′-phenylethyl-γ-valerolactone*, $\begin{matrix}\mathrm{O\text{———}CO}\\ \mathrm{CHMe{\cdot}CH_2}\end{matrix}\!>\!\mathrm{CH{\cdot}CHPh{\cdot}OH}$, a pale yellow liquid, b. p. 180—183°/13 mm., from which the corresponding *silver* salt, m. p. 185°, is obtained. When distilled under greatly diminished pressure, αβ′-hydroxypropyl-γ-phenylbutyrolactone undergoes a peculiar shortening of the side-chain, which results in the formation of *γ-phenyl-α-methylbutyrolactone*, $\begin{matrix}\mathrm{CO{\cdot}CHMe}\\ \mathrm{O\text{—}CHPh}\end{matrix}\!>\!\mathrm{CH_2}$, crystals, m. p. about 60°. The *barium* salt, short, coarse crystals, m. p. (indefinite) 236—250° (decomp.), and the *silver* salt of the corresponding acid are described.

The reduction of 6-phenyl-2-methylpyridine-3 : 4-dicarboxylic acid in ice-cold alkaline solution by a large excess of sodium amalgam leads to the production of a mixture of *ε-amino-α-hydroxy-α-phenylhexane-γδ-dicarboxylic acid*,

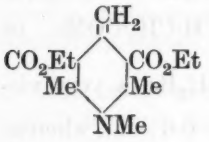
$$\mathrm{OH{\cdot}CHPh{\cdot}CH_2{\cdot}CH(CO_2H){\cdot}CH(CO_2H){\cdot}CHMe{\cdot}NH_2},$$

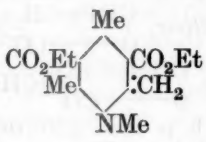
colourless needles, m. p. 260°, which readily loses water, probably with ring closure and then gives a *hydrochloride*, $C_{14}H_{17}O_4N,HCl$, long, colourless needles, m. p. 220°, and an isomeric *dicarboxylic acid*, $C_{14}H_{19}O_5N$, a colourless, extremely hygroscopic powder. H. W.

Pyridonemethides [Methylenedihydropyridines]. O. Mumm and G. Hingst (*Ber.*, 1923, **56**, [*B*], 2301—2313).—The authors have endeavoured to isolate simple members of the pyridonemethides. Since, however, these substances are expected to be highly unstable, they have chosen as initial material the readily accessible ethyl 2 : 4 : 6-trimethylpyridine-3 : 5-dicarboxylate with the object of thereby securing relative crystallisability and stability in the methide.

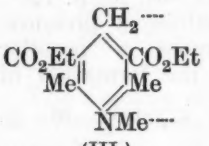
Ethyl 2 : 4 : 6-trimethylpyridine-3 : 5-dicarboxylate is readily converted by methyl sulphate into the corresponding *methosulphate*, colourless, prismatic rods, m. p. 172—174°, which is transformed by aqueous potassium cyanide solution into *ethyl 4(?2)-cyano-1-methyl-2 : 4 : 6-trimethyldihydropyridine-3 : 5-dicarboxylate*, colourless, matted needles, m. p. 92°, which decomposes when heated into

the pyridonemethide (see later). The methosulphate is transformed by 2*N*sodium hydroxide solution into *ethyl trimethylmethylene-dihydropyridine*-3 : 5-*dicarboxylate* (annexed formulæ, I and II),

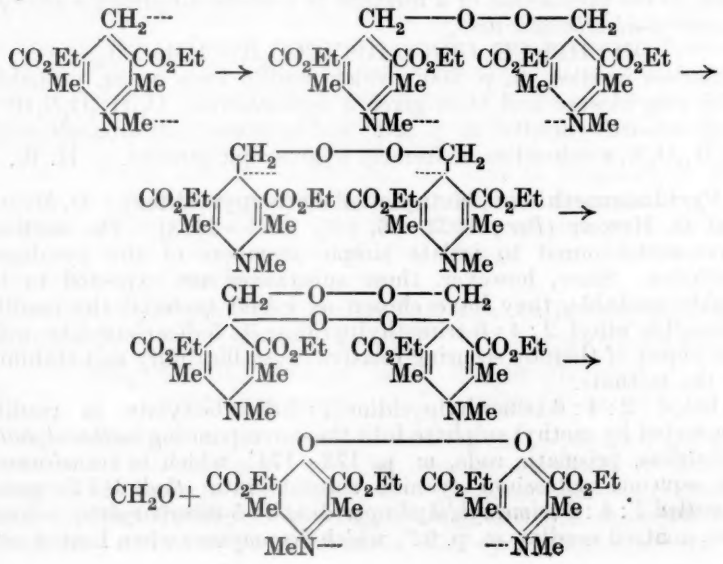

(I.)


(II.)

which is obtained in two interconvertible forms, yellow needles and yellowish-red plates, m. p. 74—75° when slowly heated; the prismatic variety is the more stable. The corresponding *perchlorate*, colourless, prismatic rodlets, m. p. 141°, and the *picrate*, yellow, prismatic crystals, m. p. 131—132°, are described. The substance is converted by methyl hydrogen sulphate into the methosulphate of ethyl 2 : 4 : 6-trimethylpyridine-3 : 5-dicarboxylate, m. p. 172—173°. It combines with iodine to give the *di-iodo*-derivative, $C_{15}H_{21}O_4NI_2$, a reddish-brown solid which could not be recrystallised. In its chemical activity, the pyridonemethide resembles closely the diarylquinonemethides, and for this reason the radicle formula


(III.)

(III) is also possible. The chemical behaviour is most easily explicable on the assumption that it is an equilibrium mixture of forms I and III. It is oxidised on exposure to air in the solid condition, more rapidly in solution to a *dipyridone*, $(C_{14}H_{19}O_5N)_2$, a hygroscopic, amorphous, brownish-black powder which yields dark red solutions. Since the pyridones described previously do not show any tendency towards polymerisation, the dipyridone must be regarded as a primary product. The course of the change is very probably represented by the scheme :



The hypothesis is in harmony with the amount of oxygen absorbed, and the intense colour of the compound is explained by the presence of the two quadrivalent nitrogen atoms of which the free valencies partly saturate one another.

The pyridonemethide adds smoothly two atomic proportions of hydrogen in the presence of hexane and spongy platinum, and is converted thereby into the unsymmetrical *ethyl* 1 : 2 : 4 : 6-*tetramethyldihydropyridine*-3 : 5-*dicarboxylate* (annexed formula), a yellow liquid, b. p. 145—155°/0·2 mm. It appears in this case to function as an α-pyridonemethide. The dihydro-compound is hydrogenated in glacial acetic acid solution to *ethyl* 1 : 2 : 4 : 6-*tetramethyltetrahydropyridine*-3 : 5-*dicarboxylate*, a pale yellow, mobile liquid, b. p. 115—122°/0·3 mm. Cautious hydrolysis of pyridonemethide by 2*N*-sodium hydroxide at the atmospheric temperature leads to the formation of ethyl 3-acetyl-1 : 4 : 6-trimethylpyrid-2-one-4-carboxylate (annexed formula), colourless, lustrous leaflets, m. p. 90·5—91°, which is transformed successively into the corresponding *carboxylic acid*, rhombic plates, m. p. 221°, and 3-acetyl-1 : 4 : 6-trimethylpyrid-2-one. The first and third of these compounds appear to be identical with the "*N*-methyldicarbocollidiniumdehydride" and "*N*-methylcarbocollidiniumdehydride" isolated by Hantzsch from the methiodide of ethyl 2 : 4 : 6-trimethylpyridine-3 : 5-dicarboxylate. The constitution of these compounds is deduced from the observation that they are converted by concentrated sulphuric acid at 180—220° into 1 : 4 : 6-trimethylpyrid-2-one, colourless, rhombic plates, m. p. 84—85°, which is further identified as the dibromo-compound, $C_8H_9ONBr_2$, colourless crystals, m. p. 169° (cf. Simonsen and Nayak, T., 1915, **107**, 792). Their formation is explained by assuming that the action of the sodium hydroxide causes a temporary fission of the ring with the production of a β-ketonic acid, from which a cyclic compound is again formed with co-operation of the terminal carboxy-group. H. W.

An Application of the Colorimetric Law of Dilution. J. Piccard and J. H. Dardel (*Ber.*, 1923, **56**, [*B*], 2253—2254).—The application of the colorimetric dilution law (cf. Piccard, A., 1911, ii, 561) to the reduction product of benzylpyridinium chloride (cf. Emmert, A., 1920, i, 331) has been effected in the expectation that an equilibrium of the type quadrivalent nitrogen ⇌ tervalent carbon would not be disturbed by dilution, whereas an equilibrium of the kind radicle ⇌ double molecule would be displaced in the customary manner. Since the intensity of the colour is not diminished by cooling the solutions to −20°, it appears impossible to regard the coloured compounds as compounds with free valencies. This conclusion has been drawn independently by Emmert (A., 1922, i, 1064; 1923, i, 383). H. W.

Isatin-4-carboxylic Acid. J. von Braun and G. Hahn (*Ber.*, 1923, **56**, [*B*], 2343—2347).—The ready preparation of the nitro-

phthalonic acid (von Braun, this vol., i, 48) has led the authors to an extended investigation of isatin-4-carboxylic acid which closely resembles isatin except in that it gives derivatives which dissolve in alkali.

Isatin-4-carboxylic acid, $CO_2H\cdot C_6H_3<\begin{matrix}CO\\NH\end{matrix}>CO$, decomp. above 200°, is readily prepared by the reduction of nitrophthalonic acid in alkaline solution by ferrous hydroxide; the bluish-black *disodium* salt and the *ethyl* ester, yellow leaflets, m. p. 140°, are described. Somewhat unexpectedly, it is converted by an excess of phosphorus pentachloride into *isatincarboxyl chloride*, $C_9H_4O_3NCl$, a black powder. *Isatin-4-carboxylic acid β-phenylhydrazone* crystallises in orange-coloured needles, decomp. 200°; the *β-anil*, a Bordeaux-red, crystalline powder, decomp. above 200°, and the yellow *β-oxime*, decomp. above 200°, are described. Isatin-4-carboxylic acid is converted by *o*-phenylenediamine into the quinoxaline derivative, $\begin{matrix}C_6H_3(CO_2H)\cdot C{:}N\\NH\text{———}C{:}N\end{matrix}>C_6H_4$, the *monosodium* and *disodium* salts of which are described. *Dioxindole-4-carboxylic acid*,

$$CO_2H\cdot C_6H_3<\begin{matrix}CH(OH)\\NH\end{matrix}>CO,$$

an almost colourless substance, decomp. above 200°, is prepared by the reduction of isatin-4-carboxylic acid with sodium amalgam by which it is reduced further to *oxindolecarboxylic acid*,

$$CO_2H\cdot C_6H_3<\begin{matrix}CH_2\\NH\end{matrix}>CO,$$

decomp. above 280°. The latter acid, together with isatin-4-carboxylic acid, is obtained when an alcoholic solution of dioxindolecarboxylic acid is boiled.

Acetophenone readily condenses with isatin-4-carboxylic acid in the presence of alkali to give *atophancarboxylic acid* (*2-phenylquinoline-4 : 5-dicarboxylic acid*), slender, colourless crystals (the *potassium* salt is described). The acid passes readily into the corresponding *anhydride*, yellow needles, m. p. 226°. Indoxyl and isatin-4-carboxylic acid give *indirubincarboxylic acid*,

$$C_6H_4<\begin{matrix}CO\\NH\end{matrix}>C{:}C<\begin{matrix}CO\text{————}\\C_6H_3(CO_2H)\end{matrix}>NH,$$

bluish-black crystals with a coppery reflex, which is decomposed by molten alkali into a *substance*, $C_{17}H_{12}O_5N_2$, decomp. above 270°. Isatin-4-carboxylic acid and thionaphthen give the *compound* $C_6H_4<\begin{matrix}CO\\S\end{matrix}>C{:}C<\begin{matrix}CO\text{————}\\C_6H_3(CO_2H)\end{matrix}>NH$, dark red crystals. H. W.

Tri-indolylmethanes and Aldehydes, Ketones, Ketonic Esters, and Keto-nitriles of Substituted Indoles. Hans Fischer and K. Pisbor (*Ber.*, 1923, **56**, [*B*], 2313—2319).—The ready applicability of Gattermann's aldehyde synthesis and of Hoesch's ketone synthesis to substituted pyrroles (A., 1922, i, 758, 1055) has led the authors to utilise these methods with substituted indoles.

A solution of 2-methylindole and chloroacetonitrile in anhydrous chloroform is converted by dry hydrogen chloride into the *ketimine*

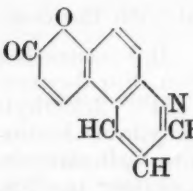
hydrochloride, m. p. 170°, which is hydrolysed to 3-chloroacetyl-2-methylindole, $NH<^{C_6H_4}_{CMe}>C\cdot CO\cdot CH_2Cl$, identical with the compound described by Salway (T., 1913, **103**, 351). It is converted by potassium cyanide in aqueous alcoholic solution into 3-*cyanoacetyl*-2-*methylindole*, small, yellow leaflets, m. p. 184°. 2-Methylindole is similarly transformed successively by anhydrous hydrocyanic acid and hydrogen chloride into the *imine hydrochloride*, m. p. about 180°, and 2-*methylindole*-3-*aldehyde*, slender needles, m. p. 198°. In like manner, ethyl indole-2-carboxylate, m. p. 119°, gives *ethyl* 3-*aldehydoindole*-2-*carboxylate*, pointed prisms, m. p. 185°, which is hydrolysed to 3-*aldehydoindole*-2-*carboxylic acid*, colourless leaflets, m. p. 247°. The ester is converted by hippuric acid in the presence of acetic anhydride and anhydrous sodium acetate into the corresponding *azlactone*, $C_{21}H_{16}O_4N_2$, yellow needles, decomp. 242°. The action of ethyl cyanoacetate on 2-methylindole in the presence of chloroform and gaseous hydrogen chloride leads to the isolation of the very stable *imine* of *ethyl* 2-*methylindole*-3-*acetate*, $C_{14}H_{16}O_2N_2$, small, colourless prisms, m. p. 151°, which does not appear to be converted into the corresponding ketonic ester even when warmed with sodium hydroxide solution. 2-Methylindole is transformed by two molecular proportions of acetonitrile into the *imine hydrochloride*, needles, and subsequently into 3-acetyl-2-methylindole, m. p. 195°.

A mixture of 3-aldehydo-2-methylindole and 2-methylindole is converted by alcoholic potassium hydroxide solution into trimethyltri-indolylmethane, colourless crystals, m. p. 319°, which is identical with the substance isolated by Ellinger and Flamand (A., 1914, i, 881). The constitution of the compound is established by the observation that it is converted by perchloric acid into 2-methylindole and di-indolylmethene perchlorate, m. p. 248°.

H. W.

Skraup's Quinoline Synthesis applied to 6-Aminocoumarin. H. KONDO and TETSUKICHI UI (*J. Pharm. Soc. Japan*, 1923, No. **498**, 615—628).—6-Nitrocoumarin was prepared by adding nitric acid (25 g., *d* 1·51) to a solution of coumarin (25 g.) in concentrated sulphuric acid (50 c.c.), the yield being 90%. It was then reduced electrolytically to 6-aminocoumarin, using a perforated copper plate as an electrode, current density 6—7 amperes, and 2·5—3·0 volts, the yield being 66%. When a mixture of 6-aminocoumarin (5 g.) and concentrated sulphuric acid (25—30 g.) is heated with glycerol (12 g.), nitrobenzene (2·7 g.), and fuming sulphuric acid (7—8 g.) in a reflux apparatus, the first violent reaction occurs at 120—135° and the second at 180—190°. The condensation product, *coumaroquinoline*, forms slightly brown needles, m. p. 232° (*mercurichloride*, colourless, hexagonal plates, m. p. 213°; *potassium chromate* compound, orange-yellow, rhombic plates; *chloroaurate*, yellow, short needles, m. p. 207°; *chloroplatinate*, orange-red, short needles, m. p. 286—290° [decomp.]; *picrate*, yellow, long needles, m. p. 214° [decomp.]). By the use of arsenic acid instead of nitrobenzene,

a purer compound is obtained. The annexed formula is ascribed to coumaroquinoline (cf. Marckwald, A., 1893, i, 603; 1894, i, 474; Claus, A., 1894, i, 174; 1898, i, 333).



By heating coumaroquinoline with methyl iodide in a sealed tube at 100° for three hours, the *methiodide*, $C_{12}H_{17}O_2N,MeI$, orange-red, rhombic plates, m. p. 252° (decomp.), was obtained; it gave the *methylate*, $C_{12}H_{17}O_2N,MeOH$, a brown syrup, on treatment with freshly prepared silver hydroxide. The *methochloride*, $C_{12}H_{17}O_2N,MeCl$, light yellow, long needles, m. p. 236° (decomp.), gave a *chloroplatinate*, orange-brown, long prisms, m. p. 250° (decomp.); *chloroaurate*, yellow, hexagonal, long prisms, m. p. 206°; *mercurichloride*, colourless, thin needles, m. p. 236° (decomp.); and *picrate*, yellow, hay-like crystals, m. p. 214° (decomp.).

By heating coumaroquinoline with concentrated hydrochloric acid and tin on a water-bath, a *tetrahydro-compound*, yellow, rectangular plates, m. p. 143°, was formed, the four hydrogen atoms being added to the pyridine nucleus. The tetrahydro-compound gave an *acetyl* derivative, colourless, rhombic plates, m. p. 149—149·5°; and a tertiary *amine*, a volatile oil, b. p. 263—265°, when heated in a sealed tube with hydrogen iodide and red phosphorus. Coumaroquinoline, when heated with 0·2*N*-alcoholic potash, did not react, whilst tetrahydrocoumaroquinoline by the same treatment gave 6-hydroxy-tetrahydroquinoline-5-acrylic acid,

$$OH\cdot C_9NH_9\cdot CH{:}CH\cdot CO_2H,$$

white, hay-like crystals, which did not melt below 285°. K. K.

Preparation of Condensation Products of the Aromatic Series containing Nitrogen and Sulphur. Leopold Cassella & Co. (D.R.-P. 370854; from *Chem Zentr.*, 1923, iv, 538—539; cf. A., 1923, i, 917).—Sulphur monochloride in excess is allowed to act at temperatures not exceeding 50° on aromatic amines containing an alkyl group in the para-position, or on salts of such amines. The reaction is allowed to take place in a solvent or diluent which is indifferent to sulphur monochloride, preferably a nitrohydrocarbon, acetic acid, or anhydrous formic acid. By the action of sulphur monochloride on *p*-toluidine in nitrobenzene solution at 15—40°, a *condensation product* is obtained which gives an orange-yellow picrate. From the hydrochloric acid solution after neutralisation with sodium acetate, or alkali hydroxides, a *compound*, $R<\begin{matrix}NH\\S\end{matrix}>SO$, separates on keeping. It condenses with chloroacetic acid, giving p-*toluidine*-o-*thiolacetate*; the inner *anhydride* has m. p. 152°. *m*-Xylidine yields similarly a *condensation product* which gives an orange-yellow, crystalline *picrate*. m-*Xylidine* o-*thiolacetate*, obtained therefrom, gives an inner *anhydride*, m. p. about 160°. Compounds of the formula given above on treatment with alkalis give *o*-aminothiophenols.

G. W. R.

The Preparation and Properties of 1-Thiolbenzthiazole, its Homologues and Derivatives. L. B. SEBRELL and C. E. BOORD (*J. Amer. Chem. Soc.*, 1923, **45**, 2390—2399).—Thiolbenzthiazole, and its derivatives, may be prepared by heating with sulphur at 206—293°, (*a*) the corresponding diarylthiocarbamide (cf. Romani, A., 1922, i, 467; also Bruni and Romani, *Giorn. Chim. Ind. Appl.*, 1921, **3**, 351), (*b*) the zinc salt of the corresponding aryldithiocarbamic acid, (*c*) the ammonium salt of the acid, (*d*) a mixture of carbon disulphide and the relevant arylamine. Bruni and Romani (*loc. cit.*; cf., also, A., 1921, i, 734), who also use phenylthiocarbamide or methyleneaniline, suppose that phenylthiocarbimide is first produced. They do not, however, take into account the concurrent production of an alkali-insoluble substance, which, in fact, they did not further investigate. This is now shown to be 1-anilinobenzthiazole (Hofmann, A., 1887, 823); it is formed in greatest quantity (16·5% theory) when thiocarbanilide is used, the simultaneous yield of thiolbenzthiazole being 73·3%. Thus a large proportion of starting material is accounted for. Moreover (Jacobson and Frankenbacher, A., 1891, 1048), 1-anilinobenzthiazole is not formed by the action of aniline on the 1-thiol derivative. It is considered that essentially the same mechanism will satisfactorily explain the concurrent production of 1-anilino- and 1-thiol compounds. The tautomeric thiol form of thiocarbanilide should exist in geometrically isomeric forms. Sulphurisation of the *trans*-form, $\begin{matrix}\mathrm{NHPh{\cdot}C{\cdot}SH}\\ \|\\ \mathrm{N{\cdot}Ph}\end{matrix}$, and subsequent elimination of hydrogen sulphide, will yield 1-anilinobenzthiazole, whilst sulphurisation of the *cis*-form, $\begin{matrix}\mathrm{NHPh{\cdot}C{\cdot}SH}\\ \|\\ \mathrm{Ph{\cdot}N}\end{matrix}$, and the removal of aniline, will give 1-thiolbenzthiazole. Also, a greater yield of the latter is obtained from phenyldithiocarbamic acid or its salts (75—80%) than from phenylthiocarbimide (60%). It is therefore likely that phenyldithiocarbamic acid (or its derivatives) also undergoes direct sulphurisation, the appropriate hydrosulphide being then eliminated. It is improbable that thiocarbanilide is an intermediate stage when dithiocarbamates are used, because this would be expected to yield a greater quantity of alkali-insoluble residue than is actually obtained.

Losanitch's work (A., 1892, 55) on the ammonium salts of aryldithiocarbamic acids is confirmed. The zinc salts are obtained in a purer form by the action of aqueous or ammoniacal zinc acetate on the ammonium salts than by adding zinc oxide to a mixture of the amine and carbon disulphide (Krulla, A., 1913, i, 1174). Zinc salts of the thiolbenzthiazoles are prepared either by the interaction of the ammonium salt and ammonium zincate in aqueous solution, or by the action of a zinc salt on the thiazole in aqueous-alcoholic solution. Normal lead salts are obtained by the action of a lead salt on the thiazole in aqueous-alcoholic solution; or an aqueous solution of its sodium salt may be used. The action of lead hydroxide on the thiazole in alkaline solution gives the basic lead salt.

Disulphides are prepared from 1-thiolbenzthiazole and its derivatives by the action of alcoholic iodine, with or without the addition of alkali (cf. Hofmann, *loc. cit.*).

1-Thiolbenzthiazole is prepared by the methods given above, in the yields, (*a*) 74·0%, (*b*) 77·5%, (*c*) 74·0%, (*d*) 76·6%. It gives an amorphous, slightly yellow disulphide, m. p. 176°, a white, amorphous *zinc* salt, a bright yellow *normal lead* salt, and a white, amorphous *basic lead* salt. 1-Thiol-3-methylbenzthiazole, white needles, m. p. 186°, is obtained in the following yields: (*a*) 49·0%, (*b*) 37·0%, (*c*) 67·0%, (*d*) 45·5%. It gives a *disulphide*, white needles, m. p. 162°, a white, amorphous *zinc* salt, a yellow, amorphous *normal lead* salt, and a white, amorphous *basic lead* salt. 1-Thiol-4-methylbenzthiazole, pale yellow plates, m. p. 163° (*disulphide*, white plates, m. p. 195°), is obtained by the method (*c*) in 69·5% yield. 1-Thiol-5-methylbenzthiazole, very pale yellow crystals, m. p. 181° (*disulphide*, white needles, m. p. 201—202°, white, amorphous *zinc* salt), is obtained in the yields (*a*) 68·0%, (*c*) 71·5%, (*d*) 57·9%.

1-*Thiol*-3 : 5-*dimethylbenzthiazole*, pale yellow crystals, m. p. 250·5°, *disulphide*, slender, white needles, m. p. 193°, is obtained in the yields (*a*) 17·2%, (*b*) 32·4%, (*c*) 34·5%, (*d*) 30·4%.

1-*Thiol*-5-*ethoxybenzthiazole*, long, cream-coloured needles, m. p. 198°, is obtained in the yields (*a*) 58·4%, (*b*) 59·3%, (*c*) 73·0%, (*d*) 55·6%, but only the third method gives a product that can be purified readily.

1-*Thiol*-5-*methoxybenzthiazole*, pale yellow needles, m. p. 201°, is prepared by any of the four methods, but is always difficult to purify; the yield by the fourth method is 62·0%.

Attempts to prepare substituted thiolbenzthiazoles from *o*-anisidine, *o*- or *p*-chloro- or -bromo-aniline, and from *p*-aminophenol, have been unsuccessful. Benzidine and carbon disulphide give a product, m. p. above 250°, which is insoluble in alkali.

W. S. N.

Constitution of Antipyrine. H. Thoms and J. Schnupp (*Annalen*, 1923, **434**, 296—312).—Of the two formulæ proposed for antipyrine, that usually accepted and due to Knorr is now shown to be correct, whereas the phenol-betaine formula of Michaelis (cf. A., 1902, i, 305) is definitely misleading. This has been shown by studying the catalytic hydrogenation of antipyrine and related compounds. It is found that whilst 2-methyl-5-pyrazolones resist hydrogenation (evidence of strong valency interaction between positions 2 and 5), hydrogenation can be effected under certain conditions, whereas if the Michaelis formula were correct, simple hydrogenation such as occurs (at the 3 : 4-position) would be extremely unlikely, although to be anticipated on the basis of the Knorr formula.

Whilst hydrogen and palladium (Willstätter) and hydrogen and colloidal palladium (Skita) effected no reduction of antipyrine, even at high pressures, this substance was readily reduced by the Sabatier–Senderens method at 160—180° to give 1-phenyl-2 : 3-di-

methyl-5-pyrazolidone, whilst at 180—220°, 1-phenyl-2 : 3-dimethylpyrazolidine was obtained.

Pyrazole and 1-phenylpyrazole are readily converted into the corresponding pyrazolines by Willstätter's method at the ordinary temperature, the conversion of the phenyl compound so obtained into the phenylpyrazolidine requiring a temperature of 70—80°. 1-Phenyl-3-methylpyrazoline, readily formed by the reduction of the corresponding pyrazole, is less easily reduced than phenylpyrazoline to the pyrazolidine.

1-Phenyl-5-pyrazolone is reduced (at 70—80°) by the Willstätter method, giving 1-phenyl-5-pyrazolidone, 1-phenyl-3-methyl-pyrazolone undergoing the corresponding reduction less rapidly. 1-Phenyl-2-methyl-5-pyrazolone is not reduced under similar conditions.

Nitrosoantipyrine is so rapidly reduced to 4-aminoantipyrine (Willstätter method) that any molecular instability induced by the nitroso-group could not be detected.

1-Phenyl-3 : 4 : 4-trimethyl-5-pyrazolone differs from other pyrazolones in being reducible (at the ordinary temperature and 860 mm.) to 5-hydroxy-1-phenyl-3 : 4 : 4-trimethylpyrazoline. In 4-keto-1-phenyl-3-methyl-5-pyrazolone, however, the 4- and not the 5-carbonyl group is reduced (the product being 4-hydroxy-1-phenyl-3-methyl-5-pyrazolone), which is additional evidence of the interaction of groups in the 2 : 5-positions.

Knorr's conception of the antipyrine molecule (" half-benzene " formula, etc.) also falls in line with the instability of 3 : 4-additive compounds. Antipyrine dibromide readily loses hydrogen bromide, giving 4-bromoantipyrine. Nitrogen peroxide, when added to a solution of antipyrine in light petroleum, gives a brown, crystalline *additive* compound, which with water affords nitroso- and nitro-antipyrine. Similarly, cyanogen bromide combines with antipyrine in ethereal solution to give an *additive* compound, decomposed by water to give 4-bromoantipyrine. E. E. T.

Synthesis of Pyrazolealdehydes. I. C. A. Rojahn and K. Fahr (*Annalen*, 1923, **434**, 252—264).—Whereas six of the best-known methods for the preparation of an aldehyde from the corresponding acid proved valueless in the pyrazole series, the method of Rosenmund (A., 1921, ii, 320) gave good, although variable, results. It was found that a catalyst " regulator " was unnecessary, the use of dry hydrogen free from oxygen being, however, essential. In presence of traces of oxygen, acid anhydrides were obtained instead of aldehydes.

5-*Chloro*-1-*phenyl*-3-*methylpyrazole*-4-*aldehyde*, colourless needles, m. p. 142—143° (*phenylhydrazone*, m. p. 174°; *semicarbazone*, m. p. 214—215°) was obtained in small quantities by the Étard oxidation of 5-chloro-1-phenyl-3 : 4-dimethylpyrazole, and in good yield by reducing 5-chloro-1-phenyl-3-methylpyrazole-4-carboxyl chloride, using a palladium–barium sulphate catalyst in presence of xylene, at 150—160°. In presence of " sulphured " quinoline and traces of oxygen, the main product was the *anhydride*, needles, m. p. 178°.

The acid gives an *ethyl* ester, m. p. 74°, an *amide*, m. p. 195°, an *anilide*, m. p. 156°, and a *dihydrazide*, $C_{22}H_{18}O_2N_6Cl_2$, m. p. 248°.

3-*Chloro*-1-*phenyl*-5-*methylpyrazole*-4-*carboxylic acid* (needles, m. p. 216°), gives an *ethyl* ester (needles, m. p. 93—94°) and a *chloride*, m. p. 67°, b. p. 235—240°/20—25 mm. The corresponding *aldehyde* (needles, m. p. 103—104°) forms a *semicarbazone* (m. p. 182°) and an *aminoguanidine* derivative (nitrate), $C_{12}H_{14}O_3N_7Cl$, m. p. 204—205° (decomp.).

1-*Phenyl*-3 : 5-*dimethylpyrazole*-4-*carboxyl chloride* has m. p. 64° and b. p. 208—210°/20 mm. The corresponding *aldehyde* forms needles, m. p. 123—124° (*phenylhydrazone*, m. p. 140—141°, *semicarbazone*, m. p. 191—192°). The acid *anhydride* has m. p. 189·5°.

1 : 3-*Diphenyl*-5-*methylpyrazole*-4-*carboxyl chloride* has m. p. 82°, and b. p. 235—240°/17 mm., the corresponding *aldehyde* (needles, m. p. 131—132°) giving a *semicarbazone* and *aminoguanidine* derivative (nitrate), $C_{18}H_{19}O_3N_7$ (m. p. 207° and 208° [decomp.], respectively), whilst the corresponding acid *anhydride* has m. p. 205°.

1-*Phenyl*-5-*methylpyrazole*-4-*carboxyl chloride* has m. p. 147° and b. p. 260—270°/25 mm., the corresponding *anhydride* having m. p. 156°. The *phenylhydrazone* of the corresponding *aldehyde* has m. p. 145° (decomp.).

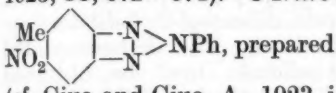
5-Chloro-1-phenyl-3-methylpyrazole-4-aldehyde, when heated with hydrazine hydrate, gave the corresponding *hydrazone*(?), m. p. 189—190°, or, at higher temperatures, the *hydrazone* of 1-*phenyl*-3-*methyl*-5-*hydroxypyrazole*-4-*aldehyde*, m. p. 201—202°, which on benzoylation gave the N-*benzoyl* derivative (m. p. 163°) of 1′-benzoyl-1-phenyl-3-methyldipyrazole (cf. A., 1917, i, 480). E. E. T.

Preparation of Unsymmetrical *C.C.*-Dialkylbarbituric Acids. E. Layraud (Brit. Pat. 191008).—New unsymmetrical *C.C.*-dialkylated derivatives of barbituric acid, viz., *ethylisobutylbarbituric* acid, *ethylisoamylbarbituric* acid, *propylbutylbarbituric* acid, *propylisobutylbarbituric* acid, and *propylisoamylbarbituric* acid can be produced by alkylising a monoalkylbarbituric acid as described in Brit. Pat. 1945/03, or by the direct condensation of carbamide or of its generators with a dialkylmalonic ester, chloride, amide, etc., in presence of a condensing agent such as a metallic alkoxide as in Brit. Pat. 1664/03, or by condensing dialkylcyanoacetic ester with carbamide or its generators in presence of an alkali alkoxide, and splitting off the imino-group by treatment with an acid as described in Brit. Pat. 18246/03. Silver ethylbarbiturate, prepared by treatment of the free acid in aqueous solution with ammoniacal silver nitrate, is heated for six hours under pressure at 150° with *iso*-butyl iodide in an alcohol solvent. The *ethylisobutylbarbituric acid* obtained has m. p. 173—174°. *Ethylisoamylbarbituric acid*, m. p. 154—155°, is similarly prepared. The former acid can also be produced by heating ethyl*iso*butylmalonic ester, carbamide, and sodium ethoxide together in alcoholic solution under pressure at 110° for five hours. *Propylbutylbarbituric acid*, m. p. 153°, is prepared by heating propylbutylcyanoethyl acetate with carbamide in alcoholic solution in presence of sodium ethoxide under reflux for six hours

and hydrolysing the sodium salt of the iminopropylbutylbarbituric acid thus produced. *Propylisobutyl-* and *isoamylbarbituric* acids, m. p. 164—165° and 134°, respectively, are similarly obtained.

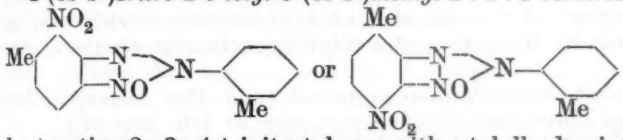
T. S. W.

Reduction of Azimino-oxides. A. ANGELETTI (*Gazzetta*, 1923, **53**, 672—674).—5-*Nitro*-2-*phenyl*-6-*methyl*-2 : 1 : 3-*benztriazole*,



(cf. Giua and Giua, A., 1923, i, 608) by means of hydrazine hydrate, crystallises in lustrous needles, m. p. 131—132°.

4-(or 1-)*Nitro*-2-*o-tolyl*-5-(or 4-)*methyl*-2 : 1 : 3-*benztriazole* N-*oxide*,



prepared by treating 2 : 3 : 4-trinitrotoluene with *o*-tolylhydrazine, crystallises in silky flocks of pale yellow needles, m. p. 202—203°, and in alcoholic solution gives with potassium hydroxide first a green and then a deep blue coloration. Saturation of its alcoholic solution with hydrogen chloride results in no coloration, although under the same conditions the nitroazo-compounds give a bright carmine-red colour (cf. Giua and Giua, *loc. cit.*). When reduced by means of hydrazine hydrate it gives 4-(or 1-)*nitro*-2-*o-tolyl*-5(or 4)-*methyl*-2 : 1 : 3-*benztriazole*, $C_{14}H_{12}O_2N_4$, which forms crystals, m. p. 164—165°, dissolves in concentrated sulphuric acid without coloration and, in alcoholic solution, gives a deep reddish-violet coloration with potassium hydroxide.

T. H. P.

Action of Acid Chlorides on Semicarbazides. E. FROMM, M. SOFFNER, and M. FREY (*Annalen*, 1923, **434**, 285—295).—A study of the action of benzoyl chloride (alone or in presence of sodium hydroxide, hot or cold), on 4-*o-tolylthiosemicarbazide* (m. p. 148°; the *benzaldehyde* and *acetone semicarbazones*, melting, respectively, at 159° and 182°) and on 4-*o-anisylthiosemicarbazide* (m. p. 156°; giving *semicarbazones* with *benzaldehyde* and *acetone*, melting, respectively, at 174° and 140°). Both thiosemicarbazides, when treated with excess of benzoyl chloride and sodium hydroxide, give, in the cold, unstable, yellow *tetrabenzoyl* derivatives (both melting at 154°). The yellow *anisyl* derivative, on crystallisation or keeping, becomes colourless, owing to decomposition; on boiling its chloroform solution and treating with alkali, it is converted into colourless *tribenzoyl*-4-*o-anisylsemicarbazide*, m. p. 136° :

$$OMe\cdot C_6H_4\cdot NBz\cdot CS\cdot NBz\cdot NBz_2 \longrightarrow OMe\cdot C_6H_4\cdot N{:}C(SBz)\cdot NBz\cdot NBz_2 \longrightarrow$$
$$OMe\cdot C_6H_4\cdot N{:}C(OH)\cdot NBz\cdot NBz_2 \longrightarrow OMe\cdot C_6H_4\cdot NH\cdot CO\cdot NBz\cdot NBz_2.$$

Tolyl- and anisyl-thiosemicarbazides give (cf. Pulvermacher, A., 1894, 304) 1-*monobenzoyl* derivatives (m. p. 138° and 157°, respectively). If the monobenzoyl–anisyl compound is heated with 1

equivalent of benzoyl chloride, or if the original thiosemicarbazide is heated with excess of this reagent, 3-*thiol*-5-*phenyl*-4-*anisyl*-1 : 2 : 4-*triazole* (m. p. 232°) is formed (*benzoyl* derivative, m. p. 176°).

If 4-*o*-tolylthiosemicarbazide is heated (1) with a slight excess of benzoyl chloride, there is obtained a *substance*, $C_{23}H_{20}ON_4S$, m. p. 188°, converted by alcoholic potassium hydroxide into potassium benzoate, and a second *substance*, $C_{16}H_{20}O_2N_4S$, m. p. 154°; whilst (2), using a large excess of benzoyl chloride, *dibenzoyl*-2 : 5-*ditoluidino*-1 : 3 : 4-*thiodiazole*, m. p. 252°, is obtained. The de-benzoylated compound, 2 : 5-o-*toluidino*-1 : 3 : 4-*thiodiazole*, may be obtained (*e.g.*, by oxidation with iodine) from *di*-o-*tolylhydrazodithiodicarbonamide*, $C_7H_7{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_7H_7$ (m. p. 179°), which is evidently formed in the above reaction by the condensation (with loss of hydrazine) of 2 mols. of 4-*o*-tolylthiosemicarbazide, and is also obtainable by the action of *o*-tolylthiocarbimide on the latter compound.

Phenyl-o-*tolylhydrazodithiodicarbonamide* and the corresponding o-*tolyl*-o-*anisyl* derivative melt, respectively, at 180° and 164°.

3-*Thiol*-4-*toluidino*-4-*tolyl*-1 : 2 : 4-*triazole* has m. p. 180° and with lead acetate gives the *compound* $C_{18}H_{14}O_2N_4SPb$, m. p. above 350°.

Di-o-*anisylhydrazodithiodicarbonamide* (from hydrazine sulphate, alkali, and anisylthiocarbimide, or from the last-named compound and anisylthiosemicarbazide) has m. p. 146°, and is converted by hot dilute sodium hydroxide into 3-*thiol*-5-*anisidino*-4-*anisyl*-1 : 2 : 4-*triazole*, m. p. 208° (*benzoyl* derivative, m. p. 192°; *mercurichloride*, m. p. above 350°), together with a little 3 : 5-*dithiol*-4-*anisyl*-1 : 2 : 4-*triazole*, isolated as the *lead* derivative.

Di-*o*-anisylhydrazodithiodicarbonamide, on oxidation with iodine, affords 2 : 5-*dianisidino*-1 : 3 : 5-*thiodiazole* (*hydrochloride*, needles; *benzoyl* derivative, m. p. 240°). E. E. T.

Action of Cyanogen Halides on Phenylhydrazine. VII. Derivatives of Guanazine. G. PELLIZZARI (*Gazzetta*, 1923, **53**, 661—667; cf. A., 1922, i, 585).—The action of cyanogen halides on phenylhydrazine yields the isomeric α- and β-cyanophenylhydrazines, $CN{\cdot}NPh{\cdot}NH_2$ and $NHPh{\cdot}NH{\cdot}CN$. The latter is readily transformed into the dimeric diphenylaminoguanazole (cf. A., 1911, i, 338), which is comparable with the so-called diphenylurazine, shown by Busch to be anilinophenylurazole (A., 1901, i, 488). It is now found that, by treatment with acetic anhydride, α-cyanophenylhydrazine may be converted into the dimeride, diphenylguanazine. This polymerisation appears to be preceded by acetylation, the first product being α-cyano-β-acetylphenylhydrazine, which then yields diacetyldiphenylguanazine, $2CN{\cdot}NPh{\cdot}NH_2 \rightarrow 2CN{\cdot}NPh{\cdot}NHAc \rightarrow NH{:}C\langle^{NPh{\cdot}NAc}_{NAc{\cdot}NPh}\rangle C{:}NH$. This compound may be de-acetylated by stages to acetyldiphenylguanazine and diphenylguanazine, and may also be acetylated further to tetraacetyldiphenylguanidine. The formation of the latter confirms the structure assumed for diphenylguanazine, but it may also react according to the tautomeric form (I), since with benzaldehyde

it yields benzylidene and dibenzylidene derivatives, to which only the formulæ II and III can be attributed :

(I.) $N\lessdot^{C(NH_2)\cdot NPh}_{NPh\cdot C(NH_2)}\gtrdot N \longrightarrow N\lessdot^{C(NH_2)\text{——}NPh}_{NPh\cdot C(N:CHPh)}\gtrdot N$ (II.) $\longrightarrow$

(III.) $N\lessdot^{C(N:CHPh)\cdot NPh}_{NPh\cdot C(N:CHPh)}\gtrdot N$

Diacetyldiphenylguanazine (see above) forms minute, lustrous, white crystals, m. p. 268°. The *monoacetyl* compound, $C_{16}H_{16}ON_6$, crystallises in tufts of silky, white needles, m. p. 228°, and exhibits slight basic properties.

Diphenylguanazine, $NH:C\lessdot^{NPh\cdot NH}_{NH\cdot NPh}\gtrdot C:NH$ or (I) (see above), crystallises in lustrous, white lamellæ, m. p. 198°, exhibits the normal molecular weight in freezing acetic acid or naphthalene, and reduces hot ammoniacal silver nitrate solution and Fehling's solution and, in alcoholic solution, cupric oxide.

Tetra-acetyldiphenylguanazine, $NAc\lessdot^{NPh\cdot C(NAc)}_{C(NAc)\cdot NPh}\gtrdot NAc$, crystallises in lustrous lamellæ, m. p. 188—189°, with previous softening.

Benzylidenediphenyldiaminodihydrotetrazine (II), forms pale yellow, lustrous crystals, m. p. 183°, and *diaminodiphenyldibenzylidenedihydrotetrazine* (III), deep yellow, lustrous needles, m. p. 150°.

T. H. P.

The Influence of Sulphur on the Colour of Azo-dyes. W. R. Waldron and E. Emmet Reid (*J. Amer. Chem. Soc.*, 1923, **45**, 2399—2417).—A number of azo-dyes containing sulphur are prepared and contrasted with similarly constituted substances not containing sulphur. The sulphur atom has a decided bathochromic effect, provided it is joined directly to the ring carrying the azo-chromophore group. If it is separated from the ring, or if it is present as a sulphone group, it has little effect.

Sodium *p*-nitrophenyl sulphide (cf. Brand and Wirsing, A., 1913, i, 406) is quite stable when pure and dry. Its preparation, and that of *p*-nitrobenzyl bromide, are described in detail.

The following p-*nitrophenyl alkyl sulphides*, $R\cdot S\cdot C_6H_4\cdot NO_2$, are prepared by the action of an alkyl halide on sodium *p*-nitrophenyl mercaptan in boiling aqueous-alcoholic solution : R=methyl, m. p. 72°, ethyl, m. p. 44°, iso*propyl*, m. p. 44·5°, β-*hydroxyethyl*, m. p. 59° (yellow needles); benzyl, *phenacyl*, m. p. 118° (yellow plates); *propyl*, d_{25}^{25} 1·1963, iso*butyl*, d_{25}^{25} 1·1573, *butyl*, d_{25}^{25} 1·1625, iso*amyl*, d_{25}^{25} 1·1335 (brown oils). The β-hydroxyethyl derivative is converted by boiling with hydrobromic acid into the β-*bromoethyl* compound, yellow plates, m. p. 58°. Esters of *p*-nitrophenyl mercaptan are obtained by the use of benzoyl chloride, carbonyl chloride, or thiocarbonyl chloride, but not of toluene-*p*-sulphonyl chloride or *m*-nitrobenzenesulphonyl chloride. The *thiobenzoate*, $NO_2\cdot C_6H_4\cdot S\cdot COPh$, yellow plates, has m. p. 123·7°; the *dithiocarbonate*, $(NO_2\cdot C_6H_4\cdot S)_2CO$, a yellow powder, has m. p. 174·5°; the *trithiocarbonate*, m. p. 141°, is a buff powder. The nitrophenyl

alkyl sulphides are reduced by means of iron dust and acetic acid, or hydrochloric acid, giving the following p-*aminophenyl alkyl sulphides*: methyl, d_{25}^{25} 1·1425, ethyl, d_{25}^{25} 1·1010, iso*propyl*, *propyl*, iso*butyl*, d_{25}^{25} 1·0421, *butyl*, iso*amyl*, benzyl, d_{25}^{25} 1·1321, which are colourless oils, but darken rapidly in the light; phenyl, m. p. 95·8°, *phenacyl*, m. p. 111·5°. The following p-*nitrophenylsulphones*, $R{\cdot}SO_2{\cdot}C_6H_4{\cdot}NO_2$, which are prepared by the gradual addition of saturated chromic acid solution to a boiling solution of the nitrothioether in 80% acetic acid, are white plates or needles: methyl, m. p. 142·5°; *ethyl*, m. p. 138·5°; iso*propyl*, m. p. 115·3°; *propyl*, m. p. 114°; iso*butyl*, m. p. 73°; *butyl*, m. p. 56·4°; iso*amyl*, m. p. 62·5°; phenyl, m. p. 142°; benzyl, m. p. 172°. Reduction of these nitrosulphones gives the following p-*aminophenylsulphones*, $R{\cdot}SO_2{\cdot}C_6H_4{\cdot}NH_2$, which are white plates or needles: R=methyl, m. p. 133°; *ethyl*, m. p. 89·3°; iso*propyl*, m. p. 122°; *propyl*, m. p. 97°; iso*butyl*, m. p. 83·7°; *butyl*, m. p. 109°; iso*amyl*, m. p. 110°; *phenyl*, *benzyl*, m. p. 218·5°.

The action of *p*-nitrobenzyl bromide in alcoholic solution at 60° on sodium methylmercaptide, or ethylmercaptide, gives *p* : *p'*-dinitrodibenzyl sulphide, but by a similar method the following sulphides are obtained: p-*nitrobenzyl butyl sulphide*, an oil, d_{25}^{25} 1·1462; p-*nitrobenzyl* iso*amyl sulphide*, an oil, d_{25}^{25} 1·1513; *phenyl* p-*nitrobenzyl sulphide*, white plates, m. p. 79°. These sulphides give, on reduction, the corresponding *aminosulphides*: *butyl*, an oil, d_{25}^{25} 1·0321; iso*amyl*, an oil, d_{25}^{25} 1·0307; *phenyl*, m. p. 72°; and, on oxidation, the p-*nitrobenzyl sulphones*: *butyl*, m. p. 139·5°; iso*amyl*, m. p. 117°; *phenyl*, m. p. 209·5°, which form white plates, and are decomposed by the action of hot 20% sodium hydroxide solution, giving a red solution and a yellow precipitate, m. p. 195°, which is free from sulphur (probably $NO_2{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}NO_2$). The p-*aminobenzylsulphones* are produced by the reduction of the nitrosulphones: *butyl*, m. p. 95°; iso*amyl*, m. p. 126°; *phenyl*, m. p. 180°, all of which form needles.

The action of sodium *p*-nitrophenyl sulphide (2 mols.) in aqueous-alcoholic solution at 65—70° on halides, such as methylene iodide, ethylene bromide, benzylidene chloride, mustard gas, or its sulphone, etc., gives p : p'-*dinitrodiphenyl* derivatives of the general formula, $(NO_2{\cdot}C_6H_4{\cdot})_2X$, where X has the structures mentioned in the following list: $-CH_2{\cdot}S-$, pale yellow plates, m. p. 108°; $-S{\cdot}CH_2{\cdot}S-$, olive plates, m. p. 179°; $-S{\cdot}[CH_2]_2{\cdot}S-$, yellow plates, m. p. 136°; $-S{\cdot}[CH_2]_3{\cdot}S-$, yellow plates, m. p. 110°; $-S{\cdot}CHPh{\cdot}S-$, yellow needles, m. p. 150·5°; $-S{\cdot}[CH_2]_2{\cdot}S{\cdot}[CH_2]_2{\cdot}S-$, yellow plates, m. p. 86·5°; $-S{\cdot}[CH_2]_2{\cdot}SO_2{\cdot}[CH_2]_2{\cdot}S-$, pale yellow plates, m. p. 170°. These give, on reduction by means of iron and acetic acid, the corresponding p : p'-*diaminodiphenyl* derivatives, which have, respectively, the following characteristics: flat needles, m. p. 93°; red needles, m. p. 99°; red needles, m. p. 111°; an oil; white needles, m. p. 131°; red needles, m. p. 93°, and white needles, m. p. 149°. Oxidation of the dinitro-sulphides by means of chromic acid in acetic acid solution gives, in general, the corresponding *dinitrosulphones*, but *p* : *p'*-dinitrodiphenyldithiomethane, $R{\cdot}S{\cdot}CH_2{\cdot}S{\cdot}R$, is broken

down into sulphonic acids : $-CH_2\cdot SO_2-$, m. p. 195°; $-CH_2\cdot SO_2\cdot CH_2-$, m. p. 260°; $-SO_2\cdot[CH_2]_2\cdot SO_2-$, m. p. 235° (decomp.); $-SO_2\cdot[CH_2]_3\cdot SO_2-$, m. p. 208°; $-SO_2\cdot[CH_2]_2\cdot SO_2\cdot[CH_2]_2\cdot SO_2-$, m. p. 235° (decomp.), of which the first forms white plates, and the others white needles. The reduction of the dinitro-sulphones presents great difficulty. The action of iron and acetic acid on dinitrodiphenylsulphone gives *p* : *p'*-diaminodiphenylsulphone (Fromm and Wittmann, A., 1908, i, 631), but from the $-SO_2\cdot CH_2-$ compound a substance is obtained, m. p. 215° (decomp.), which appears to be a nitroamino-sulphone, whilst dinitrodibenzylsulphone yields a white, tarry material. The last two reductions are, however, readily effected by the use of tin and alcoholic hydrochloric acid. p-*Aminophenyl*-p-*aminobenzyl sulphone* forms white plates, m. p. 216°; *di*-(p-*aminobenzyl*)*sulphone*, yellow needles, has m. p. 187·5°.

Dyes are prepared from the *p*-aminophenyl alkyl or aryl sulphides, the analogous sulphones, the *p*-aminobenzyl alkyl or aryl sulphides, and from the corresponding sulphones. The base, or its sulphate, dissolved in dilute hydrochloric acid, is diazotised by means of sodium nitrite at 5°. The solution, after keeping for thirty minutes, is added to a slight excess of *R*-salt, dissolved in two equivalents of sodium carbonate solution, at 5°. Dyes are made in the same way from thioanisidine or its sulphone, the following intermediates being also used : salicylic acid, Schaeffer's salt, Neville and Winther's acid, L-acid, and chromotrope acid, and these dyes are compared with those similarly derived from *p*-toluidine and *p*-anisidine. All these dyes are acid colours, dyeing animal fibres from a boiling, slightly acid bath (sulphuric acid), containing sodium sulphate. Dyes are also prepared from the *p* : *p'*-diaminodiphenyl compounds, $(NH_2\cdot C_6H_4)_2X$ (sulphides and sulphones). The base is tetrazotised at 5° as before, and, after keeping for thirty minutes, the solution is coupled at 5° with sodium salicylate (1 mol.). After keeping for three hours the liquid is warmed at 35°, and kept over-night; the second molecule of sodium salicylate is then added. These acid chrome colours are used in a boiling solution containing acetic acid and sodium sulphate, to which, if the dye is to be chromed, dichromate is subsequently added, and the boiling continued. Thioaniline, its sulphone, and the diamine from mustard gas, $(NH_2\cdot C_6H_4\cdot S\cdot[CH_2]_2\cdot)_2S$, are tetrazotised and coupled with the other intermediates mentioned above; for comparison, similar dyes are prepared from benzidine. Additional dyes are made from the same bases by tetrazotising, and coupling with H-acid, in alkaline solution, or with naphthionic acid or γ-acid, in neutral solution. These colours are applied to cotton by the use of a boiling solution containing sodium chloride.

All the dyes derived from *R*-salt and the amino-sulphides, $NH_2\cdot C_6H_4\cdot SR$, are red, except that, when R=Me or Ph, the colour is Bordeaux or scarlet. The bathochromic effect of the sulphur atom is therefore so decided that the nature of the adjacent group R makes little difference in the colour of the dye. But this is not so if the sulphur atom is removed from the benzene nucleus; for

whilst the dye derived from the base containing the group $-S\cdot CH_2Ph$ is deep red, that obtained from the isomeric base containing the group $-CH_2\cdot S\cdot Ph$ is tangerine, and so is that from the base containing $-CH_2\cdot S\cdot C_5H_{11}$ (*iso*). In the last two the oxidation of the sulphur atom to $-SO_2-$ does not alter the colour, although, in those dyes containing the $-S\cdot C_6H_4\cdot N{:}N-$ group, oxidation of the sulphur atom to $-SO_2-$ completely destroys the bathochromic effect. In fact, the sulphone group is actually hypsochromic. Thus the dyes from $NH_2\cdot C_6H_4\cdot SO_2R$ are gold coloured, whilst that from aniline and *R*-salt is orange. In this series also, the actual nature of R scarcely affects the colour. It is curious that the dye derived from the base, $NH_2\cdot C_6H_4\cdot S\cdot COPh$, is scarlet; this is ascribed to the overwhelming effect of oxidation, even of the group beyond the sulphur atom.

Since the alkyl group present in the sulphide or sulphone is of little consequence, further comparisons are made between dyes containing the groups $-Me$, $-OMe$, $-SMe$, and $-SO_2Me$. *p*-Toluidine (*a*), *p*-anisidine (*b*), *p*-thioanisidine (*c*), and its sulphone (*d*) are diazotised and coupled with salicylic acid, Schaeffer's salt, Neville and Winther's acid, *L*-acid, *R*-salt, and chromotrope acid. In the following list of colours the second refers to the chromed salicylic acid. (*a*) Yellow, yellow, orange, scarlet, red, scarlet, cardinal. (*b*) Yellow, yellow, scarlet, scarlet, red, red, heliotrope. (*c*) Yellow (darker), old gold, red, red, bordeaux, bordeaux, violet. (*d*) Gold, old gold, gold, orange, old gold, gold, red. The following order of the auxochromes mentioned, with respect to the colour of the dye, holds, therefore, regardless of the nature of the second constituent: $-SMe$, $-OMe$, $-Me$, $-SO_2Me$.

The chromed colours obtained from salicylic acid and diamines of the type $(NH_2\cdot C_6H_4)_2X$ are as follows: X=S, old gold, $-CH_2\cdot S-$ or $-CH_2\cdot S\cdot CH_2-$, old gold, $-S\cdot CH_2\cdot S-$, old gold (but deeper), $-S\cdot[CH_2]_2\cdot S-$ or $-S\cdot[CH_2]_2\cdot S\cdot[CH_2]_2\cdot S-$, gold, whilst the dye from benzidine is gold. These results also show that the sulphur atom exerts its greatest influence on colour when directly connected with the ring. The sulphone of thioaniline gives an old gold, but darker than that from thioaniline itself; the dyes from the mustard gas amine and its sulphone are practically identical.

The following colours are for the dyes derived from (*a*) benzidine, (*b*) thioaniline, (*c*) its sulphone, and (*d*) the diamine from mustard gas, when diazotised and coupled with salicylic acid (chromed), Schaeffer's salt, Neville and Winther's acid, *L*-acid, *R*-salt, chromotrope acid, γ-acid, Chicago acid, and *H*-acid: (*a*) yellow, maroon, heliotrope, claret, purple, purple, violet, purple, blue; (*b*) gold, scarlet, red, claret, claret, heliotrope, claret, lilac, purple; (*c*) gold, orange, scarlet, burnt orange, burnt orange, claret, claret, maroon, maroon; (*d*) yellow, scarlet, red, red, red, heliotrope, red, violet, lilac. In this series, the interposition of a sulphur atom, or of groups, between the benzene nuclei, destroys the mutual influence of the latter; the colours obtained are, for that reason, lighter than when benzidine is used, in spite of the effect, in series (*b*) and (*d*), of a bathochromic sulphur atom. The dyes from γ-acid and

the diamine bases having the groups $-S\cdot CH_2\cdot S-$, $-S\cdot[CH_2]_2\cdot S-$, and $-S\cdot[CH_2]_3\cdot S-$ are red, red, and maroon, respectively. That these diamine bases are unlike benzidine is illustrated by the fact that they do not form fast direct cotton dyes. The following colours refer to cotton, coloured with the dyes obtained from (*a*) benzidine, and (*b*), (*c*), (*d*), the three bases just mentioned, and naphthionic acid, γ-acid, and *H*-acid: (*a*) red, violet, blue; (*b*) burnt orange, claret, blue; (*c*) burnt orange, claret, blue; (*d*) gold, maroon, violet. W. S. N.

***J*-Acid (*iso*-γ)[6-Amino-α-naphthol-3-sulphonic Acid].** M. Battegay and A. Wolff (*Bull. Soc. chim.*, 1923, **33**, [iv], 1481—1510).—Of the forty-seven known aminonaphtholsulphonic acids, only two, *J*-acid and *M*-acid (5-amino-α-naphthol-3-sulphonic acid) yield derivatives which dye cotton fabrics directly. The authors show that *J*-acid itself and those of its derivatives in which the aminogen group is replaced by such substituents as chlorine or the hydrazine group only have a feeble affinity for cellulose, but the replacement of the hydrogen group by methylpyrazolone results in a high degree of affinity. Comparative study of the monoazo-colours derived from *J*-acid or of its derivative diazo-compounds clearly shows the great influence of the aminogen group on affinity for cellulose. The colours derived from the acid itself are more powerful dyes than those derived from the chloro- or methylpyrazolone derivatives. In replacing the amino-group by a hydrazine group the tinctorial power of the resulting substance chiefly depends on the nature of the ketone condensed with the hydrazine. Comparison with aldehydic condensation products was not possible, as the reaction stops at the intermediate stage and the final dehydration involves partial decomposition. Derivatives of aromatic α-diketones have great tinctorial power for cellulose. They may be considered as derivatives of *J*-acid in which the aminogen group is replaced by the azo-group. The authors regard them as *o*-oxyazo-dyes. The general conclusion is drawn that the derivatives of two of the many isomeric aminonaphtholsulphonic acids possess their special tinctorial properties in virtue of their more symmetrical structure.

The following derivatives of the acid are described, together with their chemical and tinctorial properties: the 4 : 4′-*tetramethyldiaminodiphenylketohydrazone*, $SO_3H\cdot C_{10}H_5(OH)\cdot NH\cdot N{:}C(C_6H_4\cdot NMe_2)_2$, an orange-red powder, prepared by direct condensation in presence of hydrochloric acid with subsequent hydrolysis of the resulting hydrochloride; the *phenanthraquinonehydrazone*,

$$SO_3H\cdot C_{10}H_5(OH)\cdot NH\cdot N{:}C_{14}H_8{:}O,$$

small, red grains, prepared as the calcium salt by condensing the hydrazine of the acid with phenanthraquinone in presence of calcium carbonate; the *isatinhydrazone*, $SO_3H\cdot C_{10}H_5(OH)\cdot NH\cdot N{:}C_8NH_5{:}O$, obtained in an impure condition as calcium salt by a similar method; 1-*sulphonaphthol*-3-*methyl*-5-*pyrazolone*,

$$\begin{matrix} CMe{=}N \\ | \\ CH_2\cdot CO \end{matrix}\!\!>N\cdot C_{10}H_5(OH)\cdot SO_3H,$$

a white powder, formed on condensing the hydrazine of the acid with acetoacetic ester, which readily couples with the diazo-compound of *p*-nitroaniline; the *tartrazine*, dark brown powder prepared from the hydrazine and sodium dihydroxytartrate; the m-*nitrobenzaldehydehydrazone*, $SO_3H{\cdot}C_{10}H_5(OH){\cdot}NH{\cdot}NH{\cdot}CH(OH){\cdot}C_6H_4{\cdot}NO_2$, orange-red, hygroscopic crystals, which do not appear to have undergone the final change involving loss of the elements of water; *sodium* 6-*chloro*-α-*naphthol*-3-*sulphonate*, white crystals; the 4-*diazo*-m-*xylidine* derivative, red powder; the 2-*diazo*-m-*xylidine* derivative of the sodium salt of 6-chloro-α-naphthol-3-sulphonic acid, orange-red powder with bronze sheen; the 4-β-*naphthylaminediazo*-derivative, small crystals with bronze sheen; the 2-β-*naphthylamine diazo*-derivative of 6-chloro-α-naphthol-3-sulphonic acid, brown powder; 6-*methylpyrazolone*-α-*naphthol*-2-*diazo*-m-*xylidine*-3-*sulphonic acid*, dark red powder; 6-*methylpyrazolone*-α-*naphthol*-2-*diazo*-β-*naphthylamine*-3-*sulphonic acid*, orange-red powder. [Cf. *B.*, 49.] H. J. E.

The Specific Ash of Proteins. R. Mieses (*Biochem. Z.*, 1923, **142**, 312—316).—A study has been made of the ash content of the various protein fractions of ox-serum. The fractions insoluble in water contain a high proportion of ash insoluble in water, whilst the reverse holds for the water-soluble fractions. In the albumin, the percentage of calcium is greater than that of phosphate; they are approximately the same in the soluble globulin, and in a reverse ratio in the insoluble globulin. J. P.

Carbophosphide and its Action on Blood-serum. G. Cuneo (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 230—237).—The passage of hydrogen phosphide through a 20% solution of carbonyl chloride in toluene results in the formation of *carbophosphide*, $CO(PH_2)_2$, as a yellow powder which has no definite melting point and decomposes at above 250°. This compound remains unaltered in either a vacuum or a desiccator, but in moist air undergoes slow oxidation with formation of carbon dioxide, gaseous hydrogen phosphide, and oxygenated phosphorus compounds.

When blood-serum is centrifuged and repeatedly filtered and then treated with about 0·4% of carbophosphide at 38—40°, a *phospho-albumin* is gradually precipitated. This compound contains phosphorus in organic combination, reddens blue litmus paper, and dissolves readily in very dilute alkali hydroxide or carbonate solution or in disodium hydrogen phosphate or sodium acetate solution. In alkaline solution, it remains unaltered for months and has a characteristic odour resembling that of ozone. It contains 14·31% N and 2·91—3·03% P, and when dissolved in 1% sodium carbonate solution and injected subcutaneously, intravenously, or intraperitoneally into the dog, produces rise in temperature.

[With E. Maragliano.]—Carbophosphide causes increased appetite in many cases, exerts an inhibiting effect in general, and especially gastro-intestinal, putrefaction, often reduces the frequency

of epileptic attacks, and is advantageous in all conditions in which administration of phosphorus is indicated. T. H. P.

Physical Chemistry of the Globulins. II. Acid Globulins. M. ADOLF (*Koll. Chem. Beihefte*, 1923, **18**, 223—274; cf. A., 1923, i, 396).—The physico-chemical relationships of the globulins have been investigated with respect to the acids, hydrochloric, sulphuric, phosphoric, oxalic, trichloroacetic, and acetic. It is shown that the different acids in the presence of an excess of albumin exhibit a definite power of dissolving globulin, which appears to be independent of the strength and basicity. None of the salts so produced is neutral but all are somewhat hydrolysed. The combining power of globulin in acid solutions is different in the different acids and is apparently not connected with the strength or basicity of the acid. It increases with acids in the order acetic < phosphoric < hydrochloric < sulphuric. In the case of the two acids last-named, the process of combination appears to be a time process. Determinations of the residual conductivity and the mobility of the ions show that there is no reason for assuming that in acid solutions further basic valencies come into action. The increased viscosity in excess of acid is not entirely dependent on the albumin concentration, for it increases with the different acids in the opposite sense to the combining power. From electrometric measurement of the hydrogen- and chlorine-ions and from residual conductivity measurements, it is shown that the viscosity maximum and the ionisation maximum coincide, and a minimum in both these factors also coincides. A correlation of the measurements shows that a portion of the acid is molecularly combined with the globulin. The quantity of combined acid is dependent on the nature of the acid anion and is inversely proportional to the hydration as determined by viscosity measurements. The ionic conductivity of the positive globulin-ion in combination with various acids has been found in excess of acid saturated with albumin to be 50 $ohms^{-1}$. In spite, therefore, of the formation of molecular compounds with acids, the globulin acid compounds behave as salts. From the present work and that previously published, globulin is found to have a valency of seven. J. F. S.

Physical Chemistry of the Globulins. III. Globulin Salts. M. ADOLF (*Koll. Chem. Beihefte*, 1923, **18**, 273—313; cf. preceding abstract).—Globulin salt solutions of high albumin content and exactly known salt concentration have been prepared, which it is shown display all the characteristic properties of natural globulin solutions. In a $N/10$-solution of an alkali chloride $3{\cdot}2\times10^{-3}$ equivalents are combined with 1 g. of globulin, hence on the basis of the previously determined molecular weight of globulin, a single molecule is combined with 4 mols. of alkali chloride. By means of electrical conductivity measurements, transport experiments, and electrometric measurements of the chloride-ion concentration, it is shown that globulin salt compounds ionise according to the equation $GM^{+}+Cl^{-} \rightleftarrows GMCl$, the ion containing the globulin being positively charged. The ionic conductivity of the positive ion of the globulin

salt is found to be 50 ohms^{-1}. The globulin salt has a not inconsiderable viscosity which is apparently independent of the nature of the anion of the salt. From electrometric measurements of the hydrogen-ion concentration, it is shown that globulin salt solutions in an excess of salt solution have a small but definite hydrogen-ion concentration which is due to hydrolysis of the globulin salt. In a solution containing 0·1*N* potassium chloride and 2·3% of globulin the degree of hydrolysis is 0·1% and is uninfluenced by a further addition of salt. The turbidity of the solution and the hydrogen-ion concentration increase with increasing dilution, and precipitation commences at a hydrogen-ion concentration 10^{-5}. The metallic portion of the salt is contained in the coagulum, hence the hydrolysis is to be expressed $GMX+H_2O \rightleftharpoons GM{\cdot}OH+HX$. Small quantities of acids precipitate globulin from globulin salts and the precipitate redissolves in an excess of acid to form an acid globulin, even in the presence of an excess of the salt. Alkali hydroxides combine with globulin salts in considerable quantities, and no precipitation takes place on progressively neutralising the alkali; the compounds thus produced behave in a manner analogous to that of the alkali globulinate solutions under similar conditions. Globulin is still to be found in solution after one-third and one-half saturation with ammonium sulphate. The so-called isoelectric point of globulin is dependent on the quantitative relations of the globulin and the buffer solution, and on the nature of the buffer solution, and indicates that value of the hydrogen-ion concentration at which the particular globulin salt ceases to have a definite existence, and the acid present is no longer sufficient to hold the globulin present in solution. The results of the present work indicate that the salt is combined with the nitrogen of the amino-group, $R(NH_2KCl){\cdot}CO_2H$. J. F. S.

Silk Fibroin. I. R. Brill (*Annalen*, 1923, **434**, 204—217).—An investigation, by *X*-ray methods, of the physical structure of fibroin from nine different sources (cf. Herzog and Jancke, A., 1921, i, 12, etc.). The interpretation of results obtained in such investigations is discussed in detail. It is concluded that fibroin is a mixture of at least two proteins, of which one is crystalline (the unit silk crystal) and is present in all the samples examined. It is suggested, among other things, that the silk protein consists of a compound formed from alanine and glycine in equimolecular proportions, these, as is indicated by the symmetry relationships observed, possibly being united to form a ring, formed of four *d*-alanylglycine anhydride groupings, combined as in a polypeptide. E. E. T.

Chemistry of Hæmoglobin. I. The Preparation of Hæmoglobin. R. M. Ferry (*J. Biol. Chem.*, 1923, **57**, 819—828).—The corpuscles from citrated horse-blood are washed six times with 1·5% sodium chloride solution and then placed in a high speed centrifuge (Sharples). The resulting paste is diluted with three to four times its own volume of water, which causes nearly complete hæmolysis, and solid sodium chloride is

then added to give a 2% solution. This is again centrifuged and the solution so obtained purified first by dialysis for three days in collodion membranes, and finally by the method of negative pressure dialysis. All the operations are carried out in a cold room at 2°. A solution of practically pure hæmoglobin, together with a crystalline deposit, is thus obtained. The freedom of the solution from other proteins may be tested by a cataphoresis method. At p_H 6·5 to 6·2 hæmoglobin and the other serum proteins migrate to opposite poles. E. S.

An Electrochemical Study of Hæmoglobin. J. B. CONANT (*J. Biol. Chem.*, 1923, **57**, 401—414).—When dipped into a solution of hæmoglobin, an inert electrode shows a fairly definite potential which varies with the degree of oxygenation. This is the oxidation–reduction potential of the system hæmoglobin–methæmoglobin. By following the change electrometrically, using potassium ferricyanide and sodium hyposulphite as oxidising and reducing agents, respectively, it has been found that the reduction of methæmoglobin involves only one hydrogen equivalent, thus suggesting that the change is from a ferri- to a ferro-compound. By passing oxygen or carbon monoxide through the system the potential is raised but is again lowered on removing the gases. These variations in the potential are due to changes in the ratio of free hæmoglobin to methæmoglobin; the conversion of hæmoglobin into oxyhæmoglobin is a process of oxygenation and not of oxidation. The author tentatively expresses the above relations between hæmoglobin, methæmoglobin, and oxyhæmoglobin by means of formulæ which emphasise the analogy between these substances and Manchot's aminoferrocyanides (cf. A., 1913, i, 1311). The reduction of hæmatin to hæmochromogen appears to involve the addition of two hydrogen atoms. E. S.

Differentiation of Oxyhæmoglobins by Means of Mutual Solubility Tests. K. LANDSTEINER and M. HEIDELBERGER (*J. Gen. Physiol.*, 1923, **6**, 131—135).—The solubilities of specimens of pure oxyhæmoglobin derived from different species are additive, which confirms the view, already suggested by serological tests, that they are different substances. C. R. H.

Distribution of Nitrogen in Globin. A. HUNTER and H. BORSOOK (*J. Biol. Chem.*, 1923, **57**, 507—514).—Using Van Slyke's method, the following results were obtained for the distribution of nitrogen in purified globin: ammonia-*N* 5·37, humin-*N* 1·90, arginine-*N* 8·0, histidine-*N* 12·7, lysine-*N* 11·1, amino-*N* of filtrate 57·0, non-amino-*N* of filtrate 3·3%. Estimations of the tryptophan and tyrosine content by Folin and Looney's method (A., 1922, ii, 539) gave values of 2·61 and 4·63%, respectively. Fürth and Lieben's method, which was used by Kiyotaki (A., 1923, i, 399) for the estimation of tryptophan in globin, is criticised. Making certain assumptions, the authors calculate from their results that the globin molecule contains 2 tryptophan, 4 tyrosine, 4 arginine, 8 histidine, 10 lysine, and about 100 other amino-acid radicles. E. S.

Is the Pentose of the Nucleotides formed under the Action of Insulin? L. B. WINTER and W. SMITH (*Nature*, 1923, **112**, 829—830; cf. A., 1923, i, 727, and Berkeley, A., 1923, i, 1259).—The substance, which responds to the α-naphthol test, but is without reducing action on copper salts, gives little indication that it contains a pentose. When the α-naphthol test is modified by the use of concentrated hydrochloric acid instead of sulphuric acid, a positive reaction is obtained only shortly after the sugar has been extracted from the tissue, and then only faintly; after some weeks, the test may fail entirely. It is believed that the substance is of a true carbohydrate nature, and its presence in normal tissues is indicated. It is pointed out that the fact that the islets of Langerhans tissue contain unusually large amounts of pentose compounds need not lead to the conclusion that the function of insulin is to convert the sugar reserves of the body into pentose derivatives. A. A. E.

Yeast-nucleic Acid. V. Methods of Preparation of Yeast-nucleic Acid. H. STEUDEL and S. IZUMI (*Z. physiol. Chem.*, 1923, **131**, 159—165).—It has been shown that yeast-nucleic acid, unlike thymus-nucleic acid, is easily decomposed by alkali at room temperature (Steudel and Peiser, A., 1923, i, 720). This makes it doubtful whether processes such as that of Altmann (*Arch. Anat. Physiol.*, 1889, 526) yield unchanged yeast-nucleic acid. Various preparations of yeast-nucleic acid have been prepared using Altmann's process, but keeping the temperature below 0°, and also by the method of Clarke and Schryver (A., 1918, i, 130), in which an extract is made with sodium chloride solution instead of with alkali. The value P/N for various fractions has been determined. It is not constant, and the variation may be due to some extent to the difficulty of working with the limited apparatus available. A value for P/N approximately equal to 1·65 has been obtained from two of the best preparations, and this agrees approximately with Levene's formula (requiring P/N=1·699). W. O. K.

Conductivity Titration of Gelatin Solutions with Acids. D. I. HITCHCOCK (*J. Gen. Physiol.*, 1923, **6**, 201—205).—The conductivity titration method of Kolthoff (A., 1920, ii, 420, 421, 501) has been applied to gelatin. The results show a combining weight of 1,160 for gelatin, which is in agreement with the value found previously by the hydrogen electrode method. C. R. H.

Density and Hydration in Gelatin Sols. T. SVEDBERG and B. A. STEIN (*J. Amer. Chem. Soc.*, 1923, **45**, 2613—2620).—The variation in density of gelatin sols in different concentrations of acetic, nitric, hydrochloric, sulphuric, and phosphoric acids has been determined. It is found that for all the acids used the density increases with an increase in hydrogen-ion concentration up to a maximum value at about p_H 5·0, after which the density curves drop toward a minimum at about p_H 4·7. The curves for the variation of viscosity of proteins with change in Sörensen values also have a maximum at p_H 3·0—3·2, dropping to a minimum at

the isoelectric point, p_H 4·7, as shown by Loeb and Pauli. The similarity of the density curves to the viscosity curves adds further verification to Pauli's hypothesis of hydration of proteins. The acids may be arranged in the following series representing their effect on the hydration of proteins; acetic < phosphoric < hydrochloric < sulphuric < nitric. It is shown that the effect of alkali and alkaline-earth chlorides on hydration is of the same order as that of the acids, and that the kations may be arranged in a series in the order of their effectiveness thus: Sr > Ca > Na,K > Li. Non-electrolytes do not affect the hydration to nearly as great an extent as do acids and salts. The anomalous action of methyl and ethyl alcohols seems to indicate that these substances favour hydration.

J. F. S.

Phthalic Anhydride as a Means of Hydrolysing Proteins. P. Brigl and E. Klenk (*Z. physiol. Chem.*, 1923, **131**, 66—96).—Treatment of ethyl phthalylglycollate, m. p. 111—113°, with concentrated aqueous ammonia results in the formation of the diamide of phthaloylglycine, fine needles, m. p. 255° (decomp.). Phthalic anhydride and glycylglycine, fused together at 200° for five minutes or at 180° for forty-five minutes, yield *phthalylglycylglycine*, thin needles, m. p. 232° (*copper* salt, bundles of needles; *ethyl* ester, fine white needles, m. p. 190°). When heated above 200°, phthalylglycylglycine decomposes, and phthalylglycine is formed. Phthalylglycylglycine along with unchanged material is also obtained from phthalic anhydride and diketopiperazine. From *dl*-leucylglycine and phthalic anhydride, *phthalyl-leucylglycine* is obtained. It is a yellow, amorphous compound, which melts indefinitely between 35° and 65°, but forms a well-defined *ethyl* ester, m. p. 126°, which on treatment with methyl-alcoholic ammonia yields the *diamide* of *phthaloyl-leucylglycine*, m. p. 211° (decomp.). When heated, this compound is converted into the *monoamide* of *phthalyl-leucylglycine*, rhombic plates, m. p. 211°.

Eighty-seven g. of elastin was heated with 130 g. of phthalic anhydride at 200° for about fifteen minutes. The excess of phthalic anhydride was removed by extraction with benzene and then with ether. The residue was dissolved in methyl alcohol and a fraction (*A*) precipitated with copper acetate. The filtrate, concentrated to a syrup, was stirred up with chloroform, thus being divided into two fractions, one soluble in chloroform (*C*), and one insoluble (*B*). Fraction (*A*) was further divided into two fractions by precipitating the copper with hydrogen sulphide and separating the fraction of the organic compound insoluble in cold water and cold alcohol, (A_1) from that soluble in cold water and cold alcohol (A_2). Fraction *C* was converted into its ethyl ester and separated into a fraction (*C*) insoluble in warm ethyl acetate, a fraction (C_1) which separates on cooling and a fraction (C_2) soluble at room temperature. Analyses of these various fractions are given. W. O. K.

The Influence of Colloids on Ferments. I. L. Pincussen (*Biochem. Z.*, 1923, **142**, 212—221).—A study has been made of the influence of colloidal iron, at varying hydrogen-ion concen-

trations, on pepsin, rennin, trypsin, malt diastase, takadiastase, and ptyalin, acting on appropriate substrates. No general rule is applicable, the results being very variable and not always in accord with the adsorption theory. In general, the colloidal iron diminished the action of the enzyme to an extent dependent on the p_H, but in certain cases an increased activity was observed. At the isoelectric point the added colloid had little or no effect on the enzyme. Indications were obtained that an enzyme may retain its activity even when adsorbed, and the interaction of the colloid and substrate may also play a part in determining the final effect.

J. P.

Amylase. L. AMBARD (*Bull. Soc. Chim. biol.*, 1923, **5**, 693—716).—A study has been made of the power of adsorbing amylase possessed by the amyloses (A., 1912, i, 832), by dextrin and by glycogen. This power increases with the molecular weight, and is taken to be a function of the grouping of the specific intra-molecular linkings of the substances concerned.

The rest of the paper is a consideration of the effect on the rate of hydrolysis of adsorption of enzyme by substrate. C. R. H.

An Amylase Preparation with Limited Powers of Hydrolysis. K. SJÖBERG (*Z. physiol. Chem.*, 1923, **131**, 116—130).—By extraction of malt with water and dialysis of the resulting solution, an enzyme has been obtained which converted only about 30% of starch into maltose. The rate of reaction is maximal at p_H 6. The presence of dextrose decreases the velocity constant of the reaction, a concentration of 3% of either sugar reducing it to about 27% of the original value. In the same way, the products of intermediate hydrolysis also exert an inhibitory action. From the hydrolysis product, a substance dialysed through a collodion membrane which produced a reddish-violet colour with iodine, presumably a dextrin. The non-dialysable part is more sparingly soluble in water than the original starch, gives a pure blue colour with iodine, and does not reduce Fehling's solution, $[\alpha]^{18°}_{Hg\ yellow}$ +158° (in 1% solution). It has some retarding influence on the hydrolysis of starch by the enzyme, and is provisionally called an amylose, but is not identical with the substance isolated by Pringsheim and Fuchs (A., 1923, i, 965). W. O. K.

The Limiting Hydrolysis of Starch and a Complement of the Amylases. II. H. PRINGSHEIM and K. SCHMALZ (*Biochem. Z.*, 1923, **142**, 108—116).—The hydrolysis of starch by maltase-free preparations of amylases (malt, salivary, and pancreatic) proceeds beyond the supposed limiting value of 70 to 78% maltose formation, and in many cases a quantitative production of the sugar has been observed. The effects of varying quantities of enzyme of different ages, and of temperature, on the extent of the hydrolysis have been studied. The complement present in yeast which accelerates the action of amylases, more particularly those of saliva and of the pancreas, on starch (cf. A., 1923, i, 965) only seems to do so above the limiting value. The complement, which is

destroyed by boiling, has a marked effect in reactivating old preparations of malt extract which have lost much of their amylolytic power. Maltose has been isolated directly in a crystalline condition from a starch hydrolysate, showing a 96% concentration of the sugar by titration. J. P.

The Influence of Colloids on Ferments. II. J. HAGIHARA (*Biochem. Z.*, 1923, **142**, 222—227).—Various preparations of pure cholesterol had no effect on the activities of different diastases between p_H 4·0 and 6·0. Between p_H 6·8 and 10·0, their activity was decreased by cholesterol. A Heyden preparation of cholesterol, which gave anomalous results, was found to contain a protective protein colloid to which the differences from pure cholesterol were traced. Lecithin, at all reactions between p_H 4·0 and 9·8 decreased the action of the diastases, with the exception that, when present in acid solution in great dilution, it was without effect. J. P.

The Differentiation of Animal and Plant Diastases. T. KOGA (*Biochem. Z.*, 1923, **142**, 159—174).—In contradistinction to diastases of animal origin, the action of those from vegetable sources (malt, takadiastase from *Aspergillus* and the diastase of *Amylomyces delamar*) is not increased by blood-serum or by sodium chloride. Yeast and malt extracts are similarly devoid of activating influences on plant diastases. On the other hand, the diastases present in *Bacillus coli* and *B. pyocyaneus* are markedly activated by blood-serum and are therefore allied to animal diastases. The use of blood-serum as a means of differentiating animal and plant diastases is suggested. J. P.

The Occurrence of Glycerophosphatase in Takadiastase. S. AKAMATSU (*Biochem. Z.*, 1923, **142**, 184—185).—Takadiastase contains a glycerophosphatase capable of hydrolysing commercial sodium glycerophosphate to the extent of 82% in twelve days. J. P.

The Hydrolysis of Lecithin by Takadiastase. S. AKAMATSU (*Biochem. Z.*, 1923, **142**, 186—187).—As in the case of synthetic glycerophosphoric acid (cf. preceding abstract), the glycerophosphoric acid residue present in egg-yolk lecithin is also hydrolysed by takadiastase. J. P.

Sulphatase. II. C. NEUBERG and K. LINHARDT (*Biochem. Z.*, 1923, **142**, 191—194).—The sulphatase found in takadiastase (A., 1923, i, 1148) hydrolyses pure potassium *p*-cresol sulphate, forming potassium sulphate and *p*-cresol. The reaction is diminished in the presence of magnesium carbonate and sodium acetate, and proceeds best in alkaline solution. Pre-war takadiastase preparations still contain active sulphatase. J. P.

Ferments and Light. III. Urease. II. L. PINCUSSEN and N. KATO (*Biochem. Z.*, 1923, **142**, 228—238).—Sunlight acting on urease solutions at p_H 6·4 diminishes the activity both of the active constituent and of "Stable Component-*X*" (cf. A., 1923, i, 1034). Potassium hydrogen phosphate at p_H 5·6 affords a partial

protection to the active component, but even in the dark the activity of the other constituent is decreased by phosphate. Ultra-violet light destroys the active enzyme both in the presence and absence of phosphate, but has not such a marked effect as sunlight in inhibiting Component-*X*. J. P.

Possible Sources of Insulin. C. H. Best and D. A. Scott (*J. Metabolic Research*, 1923, **3**, 177—179).—The presence of insulin in potatoes, rice, wheat, beet-roots, and celery was demonstrated by the preparation of extracts from these plants which when administered to rabbits caused a marked lowering of the blood-sugar. Chemical Abstracts.

Preparation of Insulin. C. H. Best and D. A. Scott (*J. Biol. Chem.*, 1923, **57**, 709—723).—The various methods which have been devised for the preparation of insulin are reviewed and the method at present in use at the University of Toronto is described. Although the preparation of insulin by extraction of the pancreas with acidified water has yielded promising results, the yields are considerably smaller than those obtained by alcoholic or acetone extraction; moreover, the aqueous extracts are more difficult to purify. E. S.

Concentration of Insulin by Adsorption on Benzoic Acid. P. J. Moloney and D. M. Findlay (*J. Biol. Chem.*, 1923, **57**, 359—361).—Impure solutions of insulin may be purified, or dilute solutions concentrated, by adsorption on benzoic acid. For this purpose, the insulin solution is treated with a solution of sodium benzoate and the benzoic acid precipitated by addition of hydrochloric acid, the process being repeated, if necessary, on the filtrate. The insulin may be recovered by suspending the precipitate in water and extracting the benzoic acid with ether. If, however, considerable amounts of impurities are present, this method of recovery is not applicable and other methods (*e.g.*, solution of the precipitate in glacial acetic acid and precipitation of the insulin in a solid form with ether) must be employed. E. S.

Action of Proteolytic Enzymes on Insulin. E. J. Witzemann and L. Livshis (*J. Biol. Chem.*, 1923, **57**, 425—435).—Insulin is inactivated by trypsin, papain, and pepsin; this indicates that it has a protein-like nature. The suggestion is made that the action of insulin is due to a particular group or grouping which may be present either in a protein, a peptone, or a polypeptide. E. S.

Preparation of Derivatives of Arsenobenzene Stable in Solution. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.P. 375718; from *Chem. Zentr.*, 1923, iv, 537).—Stable solutions of arsenobenzene derivatives may be obtained by mixing, for example, solutions of the methylene sulphoxylate and the carbamate of 4-aminoarsenophenyldimethylpyrazolone; 4-aminoarsenophenyldimethylpyrazolone carbamate, and 3 : 3′-diamino-4 : 4′-dihydroxyarsenobenzene methylenesulphoxylate; dimethylhexaminoarsenobenzene and 3 : 3′-diamino-4 : 4′-dihydroxyarsenobenzene methylene

sulphoxylate; dimethylhexaminoarsenobenzene and a mixture of the carbamate and methylene sulphoxylate of 4-aminoarsenophenyldimethylpyrazolone; 4-aminoarsenophenyldimethyl pyrazolone and the sodium salt of 4-aminoarsenophenyldimethylpyrazolone glycine. G. W. R.

Arsinated *N*-Arylamino-alcohols. C. S. HAMILTON (*J. Amer. Chem. Soc.*, 1923, **45**, 2751—2754).—Ethylene chlorohydrin and sodium *p*-arsanilate react in boiling aqueous solution to give β-p-*arsinoanilinoethyl alcohol*, $OH{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4{\cdot}AsO_3H_2$, colourless needles, m. p. 167—168°; the *sodium*, *ammonium*, and *barium* salt are described. The use of trimethylene chlorohydrin gives γ-p-*arsinoanilinopropyl alcohol*,

$$OH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4{\cdot}AsO_3H_2,$$

colourless crystals, m. p. 160—161°; the *sodium*, *ammonium*, and *barium* salts are described. These arsino-compounds are reduced by means of hot, aqueous sodium hyposulphite to give, respectively, β-p-*arsenoanilinoethyl alcohol*, $(OH{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4As{:})_2$, and γ-p-*arsenoanilinopropyl alcohol*, $(OH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4As{:})_2$, both of which are yellow compounds, which do not melt at 250°. Condensation could not be effected between a chlorohydrin and *m*-arsanilic acid, 2-amino-*p*-tolylarsinic acid, or 3-amino-4-hydroxyphenylarsinic acid. Of the two sodium salts mentioned above, the propane derivative is apparently the more toxic, and has the higher trypanocidal action.

When *p*-arsanilic acid, sodium hydroxide solution, and ethylene dibromide are boiled under reflux, the product contains, besides unchanged material, s-*di*-p-*arsinoanilinoethane*,

$$C_2H_4(NH{\cdot}C_6H_4{\cdot}AsO_3H_2)_2,$$

which does not melt at 250°, and gives a colourless, crystalline *sodium* salt. W. S. N.

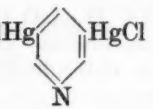
o-Amino- and o-Acetamido-phenylstibinic Acids. A. D. MACALLUM (*J. Soc. Chem. Ind.*, 1923, **42**, 468—471T).—o-*Nitrophenylstibinic acid* was prepared from *o*-nitroaniline by a slight modification of the diazo-method of Schmidt (A., 1920, i, 900). Molecular-weight determinations of this and the other compounds described, by the cryoscopic method, indicate a unimolecular structure. When boiled with an excess of sodium hydrogen tartrate, *o*-nitrophenylstibinic acid forms a *tartrate*,

$$NO_2{\cdot}C_6H_4{\cdot}SbO(OH){\cdot}C_4H_4O_6Na.$$

The acid can be reduced with ferrous sulphate or ferrous hydroxide in alkaline solution to o-*aminophenylstibinic acid*, $NH_2{\cdot}C_6H_4{\cdot}SbO_3H_2$, which forms a brown powder soluble in 200 parts of water. It forms a *lead* salt, $C_{12}H_{14}O_6N_2Sb_2Pb,8H_2O$, and a *barium* salt, $C_6H_8O_3NBaSb,4H_2O$. The amino-acid can be acetylated with acetic anhydride in neutral solution at 0° to o-*acetamidophenylstibinic acid*, which does not melt below 250°. *Di*-o-*chlorophenylstibinic acid*, $(C_6H_4Cl)_2SbO_2H$, is formed from antimony oxide and *o*-chlorodiazobenzene chloride; its *chloride* has m. p. 105—110°. The acid is sparingly soluble in alkalis. E. H. R.

Mercury Derivatives of Pyridine. G. SACHS and R. EBERHARTINGER (*Ber.*, 1923, **56**, [*B*], 2223—2226).—Mercuration of pyridine can be effected in much the same manner as that of benzene but at a somewhat higher temperature. The mercuri-complex enters in the β-position to the nitrogen atom; substitution thus proceeds in the normal manner for pyridine.

A solution of mercury acetate in pyridine is heated during two and a half hours at 175—180°, the product is dissolved in water and treated with sodium chloride whereby *pyridine-3 : 5-dimercurichloride* (annexed formula) is precipitated as a pale-brown, amorphous, odourless powder, decomp. 220°. The mother-liquors from the chloride are treated with sodium iodide, which causes the separation of *pyridine-3-mercuri-iodide*, C_5H_4NIHg, a yellow, amorphous powder, m. p. 68—69°. The constitution of the mercuri-derivatives is elucidated by converting them by means of a solution of bromine and sodium bromide into 3 : 5-dibromopyridine, m. p. 110°, and 3-bromopyridine, respectively; the latter substance is identified as the additive *compound* with mercuric chloride, $C_5H_4NBr,HgCl_2$, colourless, microscopic needles, m. p. 196—196·5°. Since, however, the yields of the bromopyridines are not quantitative, it is possible (although not probable) that isomeric mercuri-derivatives may also be produced. H. W.



Mercury Compounds of Purine Derivatives. L. ROSENTHALER and A. ABELMANN (*Ber. Deut. pharm. Ges.*, 1923, **33**, 186—190).—The following compounds are precipitated by the addition of a 10% solution of mercurous nitrate to a solution in nitric acid of caffeine, theobromine, and theophylline, respectively: *Caffeine mercuronitrate*, $C_8H_{10}O_2N_4,HgNO_3$, forms microscopic crystals which have no definite m. p. and decompose at 245—250°. The aqueous solution has a feebly acid reaction and is very sensitive towards bases, even aniline causing the liberation of mercurous oxide. The substance, from which caffeine is extracted by means of chloroform, gives all the reactions of mercurous compounds. *Theobromine mercuronitrate*, $C_7H_8O_2N_4,HgNO_3$, crystallises in prisms, which do not melt below 300°. It is sparingly soluble in cold water and, when heated with water, undergoes partial decomposition with liberation of metallic mercury. *Theophylline mercuronitrate*, $C_7H_8O_2N_4,HgNO_3$, forms amorphous masses not melting below 300°. Towards weak bases it behaves like the caffeine analogue and towards water like the theobromine compound. A different type of compound, having the formula $(C_7H_7O_2N_4)_2Hg$, is precipitated on mixing a solution of theophylline in dilute acetic acid with a cold, saturated, aqueous solution of mercuric acetate. It forms microscopic needles which do not melt below 300°, and is converted into caffeine on methylation. The corresponding derivative of theobromine is not obtainable by the above method, and caffeine, containing no free imido-hydrogen atom, is also incapable of reacting thus with mercuric acetate. W. T. K. B.

Physiological Chemistry.

The Consumption of Oxygen in Sea Organisms when exposed to the Atmospheric Air. IVAN GJAJA (*Glas. Acad. Sci. Belgrade*, **105**, 35—41).—Experiments with the sea-gastropod *Trochus* and the sea-urchin *Echinocidaris* show that both organisms are able to live a certain time when exposed to atmospheric air. The results were compared with the consumption of oxygen in some land-organisms (*Helix nemoralis*, *Rana esculenta*). The amount of oxygen consumed was found to be respectively: *Trochus* and *Helix nemoralis* 1·3 c.c., *Echinocidaris* 3·1 c.c., *Rana esculenta* 0·66—1·32 c.c. of oxygen per hour and per g. of dry organic substance. The experiments were made at approximately the same temperature.

S. S. M.

Physiology of Muscular Exercise. V. Oxygen Relationships in the Arterial Blood. H. E. HIMWICH and D. P. BARR (*J. Biol. Chem.*, 1923, **57**, 363—378).—During and after short periods of vigorous leg exercise (cf. A., 1923, i, 623, 624) there is a rise in the oxygen content, oxygen capacity, and oxygen saturation of arterial blood. The factors which cause this change are discussed in detail and the conclusion is drawn that the increased diffusion of oxygen through the lungs is mainly responsible. With longer periods of exercise it is probable that there is a decrease in the oxygen content of arterial blood owing to the continued rise in the circulation rate.

E. S.

The Transport of Carbon Dioxide in the Blood of Marine Invertebrates. T. R. PARSONS and W. PARSONS (*J. Gen. Physiol.*, 1923, **6**, 153—166).—The blood of the lower marine invertebrates can take up no more carbon dioxide than can sea-water; that of the higher forms can take up twice or three times as much. The form of the carbon dioxide dissociation curves obtained indicates that the hæmocyanin in the blood of these animals plays a similar part in the carrying of carbon dioxide to that played by hæmoglobin in the blood of vertebrates.

C. R. H.

Ether Anæsthesia. II. Anæsthetic Concentration of Ether for Dogs. E. RONZONI (*J. Biol. Chem.*, 1923, **57**, 761—788).—Using the method of Shaffer and Ronzoni (this vol., ii, 69) for the ether estimations, it has been found that during ether anæsthesia the concentration of ether in arterial blood varies directly with that in alveolar air, and depends on the distribution coefficient between air and blood at body temperature. During the induction of anæsthesia, and with a continued administration of a constant amount of ether, the concentration in arterial is greater than in venous blood. This is probably due to the great solubility of ether in the depot fat. For the same reason, the concentration is higher in venous blood during the elimination of the ether. An ether tension in alveolar air of 33—41 mm. produces respiratory failure,

in dogs when anæsthesia is induced rapidly; after several hours, a tension of 27—34 mm. is sufficient. E. S.

Distribution of Phosphorus in the Blood. T. F. Zucker and M. Gutman (*Proc. Soc. Exp. Biol. Med.*, 1922, **20**, 133—136).—Estimations made on the fresh, protein-free filtrate of human blood by Tisdall's method gave 2·66 mg. of inorganic phosphorus in a total phosphorus content of 19·43 mg. Boiling for two hours caused the hydrolysis of 9·73 mg. of the remaining phosphorus in organic combination. Chemical Abstracts.

The Inorganic Phosphorus and Calcium in Maternal and Fœtal Blood. A. F. Hess and M. Matzner (*Proc. Soc. Exp. Biol. Med.*, 1922, **20**, 75—76).—Tests were made on the maternal blood before, and forty-eight hours after, parturition, and on the cord blood of infants. The calcium did not vary significantly from the normal. The average inorganic phosphorus content for twenty-one infants was 3·71 mg.%; the mothers' blood contained 2·89 mg.% when taken from one to two days after parturition. The maternal blood during pregnancy averaged 2·77 mg.% of inorganic phosphorus for twelve individuals. The normal inorganic phosphorus content of the blood of young infants is 4·5 mg.%. The estimations were made on the whole blood by Bell and Doisy's method. Chemical Abstracts.

Rickets in Relation to the Inorganic Phosphate and Calcium in Maternal and Fœtal Blood. Al. H. Hess and M. J. Matzner (*Amer. J. Diseases Children*, 1923, **26**, 285—289).—The inorganic phosphorus of the new-born is generally lower than that of infants of one month of age or older. However, even when the percentage was within rachitic range, rickets was not evident. No relationship was found between the percentage of inorganic phosphorus in the blood of the new-born and the occurrence of rickets during the first year of life. Chemical Abstracts.

Calcium and Phosphorus in the Blood Plasma in Rickets and Tetany. J. H. Hess, J. K. Calvin, C. C. Wang, and A. Felcher (*Amer. J. Diseases Children*, 1923, **26**, 271—279).—In moderate rickets, the phosphorus, or calcium, or both, may be moderately lowered; in severe rickets the phosphorus is markedly reduced, whilst the calcium may or may not be lowered. In rickets complicated by tetany, the calcium is reduced, whilst the phosphorus may or may not be reduced. Chemical Abstracts.

Fat Transport in the Body. Changes in the Lipoid Content of the Blood and Lymph during Fat Absorption in the Dog. H. C. Eckstein (*Proc. Soc. Exp. Biol. Med.*, 1922, **20**, 74—75).—The thoracic lymph of an eighteen-hour fasting dog was collected before and after the introduction of olive oil into the duodenum. The total fatty acids increased rapidly during fat absorption; the phosphatides remained unchanged. Phosphatides were not synthesised during the passage of the fat components through the intestinal wall. Chemical Abstracts.

Insulin and Glycolysis. G. S. Eadie, J. J. R. Macleod, and E. C. Noble (*Amer. J. Physiol.*, 1923, **65**, 462—476).—Insulin added to defibrinated blood (dog and rabbit) in vitro, or injected into the animals previously to drawing the blood, does not accelerate the rate of glycolysis in the blood samples. In mixtures of blood, muscle juice, and phosphates, insulin decidedly retarded glycolysis, whereas Cohnheim's extract of pancreas had no influence. The action of insulin is thought to be an extravascular or intracellular process. Chemical Abstracts.

Changes in the Permeability of Red Blood-corpuscles in Non-electrolytic Solutions. R. Höber and A. Memmesheimer (*Pflüger's Archiv*, 1923, **198**, 564—570; from *Chem. Zentr.*, 1923, iii, 686).—Red blood-corpuscles washed with an isotonic solution show decreased absorption of "vital colouring" ("vital färbender") basic dyes in comparison with corpuscles washed with isotonic sodium chloride solution of the same reaction. The difference is not observed with "non-vital colouring" acid dyes. Glycine has the same inhibitory effect on dye absorption as sugar.

G. W. R.

The Distribution of Chlorine in the Blood. L. Csáki (*Biochem. Z.*, 1923, **142**, 360—369).—The average chloride content of red blood-corpuscles is 60% of that of the plasma, the extreme values found, including both normal and pathological cases, being 43% and 78%. A similar difference is shown by defibrinated and hirudin blood. The chloride content of both native and hirudin serum after spontaneous coagulation is the same as that of the corresponding plasma, but a marked alteration in the distribution of the chlorine occurs after defibrination, on passing carbon dioxide, and on previously administering large doses of sodium hydrogen carbonate. Corpuscles from defibrinated blood, in contact with isotonic sodium sulphate or dextrose solutions, lose chloride and after some hours the external solution contains more than the corpuscles (cf., also, A., 1922, i, 1086). J. P.

Does Dextrose in Blood Undergo Modification by other Blood Constituents before Oxidation in the Tissues? T. Büdingen (*Z. Klin. Med.*, 1923, **97**, 147—168; from *Chem. Zentr.*, 1923, iii, 634).—The combustion of dextrose is facilitated by preliminary moistening with blood. It is supposed that by reaction of dextrose with mineral salts in blood, "dextrates" are formed which are more readily combustible than the sugar itself. It is suggested that such dextrates occur in blood. Proteins and certain amino-acids such as tyrosine, leucine, glycine, and aspartic acid also increase the combustibility of dextrose. Iron compounds containing hydroxyl groups show a similar effect, but iron and iron oxides are without effect. The rate of oxidation of sugar in blood is increased by the addition of certain salts, whilst under pathological conditions the rate of oxidation may be diminished. The increase in the respiratory quotient after injection of dextrose is held to be due to the blood-sugar becoming more readily oxidised through reaction with the kations present. G. W. R.

The Potassium Content of Human Serum. L. WILKINS and B. KRAMER (*Arch. Intern. Med.*, 1923, **31**, 916—922).—Normal human serum contains 18—22 mg. of potassium per 100 c.c. Increases were observed only in nephritis (25—26 mg.) and in tetany (23—29 mg.). There was no apparent relation between an increased potassium and a decreased calcium content. The ingestion of 1·3 g. of potassium iodide three times daily for a long time did not increase the potassium content of the serum, but after the ingestion of 2, 10, and 15 g. of potassium chloride, the potassium content of the serum was increased to 25, 30, and 35 mg., respectively, in about two hours, with subsequent return to normal.

CHEMICAL ABSTRACTS.

Mode of Occurrence of Proteins in Plasma and Serum. I. Are Serum Proteins combined with Alkalis? R. MOND (*Pflüger's Archiv*, 1923, **199**, 187—193; from *Chem. Zentr.*, 1923, iii, 570).—In normally reacting blood only a very small proportion of the sodium present in the serum is combined with proteins, which are principally present in forms other than salts. A minimal buffer effect occurs between the neutral point and the isoelectric point for globulins. The buffering (? titration) curve is markedly sigmoid.

G. W. R.

The Organic Constituents of the Saliva. H. B. LEWIS and H. UPDEGRAFF (*Proc. Soc. Exp. Biol. Med.*, 1922, **20**, 168—169).—Human saliva contained approximately 30% as much uric acid as the blood; the values ranged from 0·6 to 2·9 mg. per 100 c.c. Benedict's method applied to a filtrate obtained by a modified Folin and Wu precipitation method was used. The salivary glands were not readily permeable to dextrose. CHEMICAL ABSTRACTS.

Cholesterol in Duodenal Contents. J. J. HERTZ and M. KAHN (*Proc. Soc. Exp. Biol. Med.*, 1922, **20**, 167—168).—In the fasting state, the cholesterol in the duodenal contents of different individuals varied from 25 to 105 mg. in 10 c.c. Concentrated magnesium sulphate solution introduced into the duodenum caused a rapid increase in the cholesterol content, indicating an outpouring of concentrated bile. CHEMICAL ABSTRACTS.

Fat and Protein Absorption after Comprehensive Resection of the Intestine. O. SCHUMM and A. PAPENDIECK (*Z. physiol. Chem.*, 1923, **131**, 54—59).—After resection of 3·7 m. of the intestine, about four-fifths of the fat consumed was excreted in the fæces, which also contained about two-thirds of the nitrogen in the food.

W. O. K.

Investigations on Iodine Metabolism. I. Experiments with Physiological Quantities of Iodine on Adults. T. VON FELLENBERG (*Biochem. Z.*, 1923, **142**, 246—262).—Iodine, taken in physiological quantities, is excreted chiefly by the kidney, but also in variable amounts in the fæces, nasal excrement, and in the sweat. Potassium bromide, sodium fluoride and chloride, and copious water drinking do not affect the excretion of iodine. A Turkish bath

increases the iodine excretion by the skin, but the total is not increased. Physical exercise and fevers increase the total excretion, whilst during fasting and sleeping it diminishes. Iodine equilibrium is attained on a daily intake of about 14 micrograms (cf. *Biochem. Z.*, 1923, **139**, 371). If the intake is increased, a readily mobilised "actual" reserve is built up, which is distinguished from the potential reserve of the thyroids. The course of iodine metabolism is dependent to a certain extent on the nature of the iodine compound administered, thus iodine fats are more readily absorbed than iodides. J. P.

Energetic Metabolism in Mouse and Rat. I. GJAJA and BRANDIMIR MALEŠ (*Glas. Acad. Sci. Belgrade*, **105**, 1—34).—The energetic metabolism in mouse and rat was measured by the consumption of oxygen. The first series of experiments with mice at constant temperatures showed that in the whole interval from 1·5° to 40° (the lethal temperature) the amount of oxygen consumed was almost constant from the beginning of the experiment. In a second series of experiments with mice and rats, the temperature during the experiment was changed in order to examine the influence of various temperatures on the consumption of oxygen. The consumption of oxygen increases with decreasing temperature owing to the production of complementary heat in the organism to compensate loss by radiation. A third series of experiments on mice has shown that the temperature at which the animal produces a complementary heat does not depend on the size of the animal, but depends rather on its greater or lesser protection by fur, the beginning of the production of a complementary heat being at a higher temperature in the case of a badly protected animal. S. S. M.

Metabolism of Fixed Base during Fasting. J. L. GAMBLE, G. S. ROSS, and F. F. TISDALL (*J. Biol. Chem.*, 1923, **57**, 633—695).—The discussion which is developed in this paper is based on the conception that, since the osmotic pressure and p_H of the body-fluids are to a large extent dependent on the concentration in them of total fixed base, the maintenance of an approximately constant value of the latter is the chief result of the processes of acid–base metabolism. During starvation, the following causes contribute to an increased excretion of acidic radicles: destruction of tissue protoplasm with the production of sulphuric and phosphoric acids, reduction in the total volume of the body-fluids, and the production of ketonic acids owing to the incomplete oxidation of fat. The first two processes also liberate fixed base, which is available for the excretion of acidic radicles; in addition, a certain quantity of calcium is derived from the calcium deposits of the body. The total amount of base available is, however, insufficient for the excretion of the acids produced by the above causes, and two regulatory mechanisms come into play to adjust this and so maintain the concentration of total fixed base in the plasma and, consequently, in the other body-fluids. These are, the excretion of urine of an acidity greater than that of the plasma, and the production of ammonia in the kidney. Calculations, made from estimations of the inorganic constituents

of the plasma and urine of four epileptic children undergoing periods of fast, approximately confirm these views, which are discussed in great detail in the original. E. S.

Estimation of the Alkali Retention in Growth. A. T. Shohl (*Proc. Soc. Exp. Biol. Med.*, 1922, **20**, 139—140).—The acids and bases in the food, urine, and fæces were estimated in terms of *N* solutions. The alkali retention expressed in c.c. of 0·1*N* solution per kg. of body-weight amounted to 11 c.c. in infants. Of the alkali retained, 2 c.c. was required for protein increase, 4 c.c. for the alkaline reserve, and about 57 c.c. for the formation of bone.
Chemical Abstracts.

The Physiology of Sleep. I. The Effects of Prolonged Sleeplessness on Man. N. Kleitman (*Amer. J. Physiol.*, 1923, **66**, 67—92).—Experimental insomnia in man (forty to one hundred and fifteen hours) produced no change in the blood-sugar, alkaline reserve of the blood and plasma, hæmoglobin content, or certain other factors. Increased excretion of phosphates and acids is apparently due to sleep. There is a greater excretion of chlorine in the day time; the same is true in insomnia, but there is a tendency to reversal in a subject who sleeps during the day. The excretion of total nitrogen and of creatinine shows little diurnal variation, and is unaffected by either insomnia or reversed routine.
Chemical Abstracts.

Composition of Herring Ova. III. Researches on Ova, Using Micro-methods. H. Steudel and S. Osato (*Z. physiol. Chem.*, 1923, **131**, 60—64).—Micro-estimations show that there are, in 100 herring ova, 1·546 mg. of total N, 0·0054 mg. of ammonia N, 0·1054 mg. of urea N, 0·0024 mg. of creatinine, and an amount of a reducing substance corresponding with 0·2 mg. of dextrose. The total nitrogen is 13·59% of the weight of the dried eggs, and this corresponds with the value 13·23% obtained by using micro-methods on larger quantities of eggs. W. O. K.

The Composition of Herring Ova. IV. H. Steudel and E. Takahashi (*Z. physiol. Chem.*, 1923, **131**, 99—106).—In the aqueous extract of herring ova, the following substances have been isolated and identified: guanidine, adenine, histidine, arginine, lysine, and cystine. Colour reactions indicate the presence of small quantities of tyrosine, tryptophan, and of creatinine. W. O. K.

The Composition of Herring Ova. V. The Monoamino-acids of the Skins of the Ova. S. Osato (*Z. physiol. Chem.*, 1923, **131**, 151—158).—The monoamino-acids of the skin of 38·7 g. of herring ova have been investigated, using Fischer's ester method, and the following constituents have been isolated: alanine, 0·1 g.; valine, 1·1 g.; leucine, 4·3 g.; glutamic acid, 0·16 g.; proline, 0·6 g.; tyrosine, 6·27%; cystine, 0·71%, tryptophan, 2·02%. The last three have been estimated by the method of Folin and Looney (A., 1922, ii, 539). W. O. K.

The Concentration of Various Anions and Kations in Cerebrospinal Fluid and Serum. J. B. PINCUS and B. KRAMER (*J. Biol. Chem.*, 1923, **57**, 463—470).—Analyses have been made of the serum and cerebrospinal fluid of normal and pathological subjects. The results show that, in the cerebrospinal fluid of a normal individual, the concentration of inorganic phosphorus is considerably, and of potassium somewhat, smaller than in the serum; chlorides, on the other hand, have a much higher concentration than in the serum, whilst that of sodium and of hydrogen carbonate is the same in both fluids; the concentration of calcium is 40—50% of that of the serum. The Donnan membrane equilibrium appears to be important in determining the relation between the concentration of the various constituents in the two body-fluids. E. S.

Lipase Production by the Liver. P. V. PREWITT (*Amer. J. Physiol.*, 1923, **65**, 287—295).—The isolated dog liver perfused with defibrinated dog blood may increase or decrease in lipolytic activity under various conditions. The lipolytic activity of the liver was determined by extraction with water and testing the hydrolysing power of the extract on ethyl butyrate. The lipase content of the unperfused liver is very much greater than that of the perfused organ, the marked decrease in liver-tissue following the initial perfusion not being accounted for by the slight increase in the lipase of the perfusion fluid. The addition of secretin to the perfusion fluid results in an increased lipase content of the liver-tissue. Although hepatic lipase does not seem to be increased by the action of pilocarpine, interchange of lipase between liver and blood is apparently facilitated under its influence. The lipolytic activity of the liver is not altered immediately by asphyxia, but changes are induced which are favourable to increased activity during subsequent perfusion.

CHEMICAL ABSTRACTS.

The Physiology of the Polyamyloses. II. Glycogen Formation and Animal Combustion. H. VON HOESSLIN and H. PRINGSHEIM (*Z. physiol. Chem.*, 1923, **131**, 168—176).—Perfusion of the surviving liver of the guinea-pig with a solution of maltose or of tetra-amylose does not result in the formation of glycogen. No excretion of tetra-amylose takes place after administration of tetra-amylose to the living animal, neither is there any increase of glycogen in the liver. A similar result is obtained with hexa-amylose. No increase of dextrose appeared in the urines of two diabetic patients after administration of 50 g. of tetra-amylose.

W. O. K.

Chemical Study of Several Marine Molluscs of the Pacific Coast. The Liver. P. G. ALBRECHT (*J. Biol. Chem.*, 1923, **57**, 789—794).—Analyses are presented of the liver of certain marine molluscs (abalone, Pismo clam, *Cryptochiton*, *Ischnochiton*, owl limpet). All had a relatively high iron content; creatine, creatinine, and uric acid were absent; urea was present in all except the abalone; and all contained those enzymes which are known to be present in the alimentary canal. The last result supports the view that the

enzymes have their origin in the liver. An active uricase was found in the abalone and Pismo clam. E. S.

The Effect of Quinine on the Iodine Content of the Thyroid Gland. H. SUGATA (*Amer. J. Physiol.*, 1923, **65**, 282—286).—Quinine sulphate administered to dogs (fasting or fed) in daily doses of 0·2 to 0·3 g. per kg. caused a considerable increase in the iodine content and concentration of the thyroid. High external temperature (35°) also causes an increase in iodine, whilst a decrease is produced by starvation. It is believed that endogenous protein metabolism is fundamentally responsible for the distribution of iodine in the body. CHEMICAL ABSTRACTS.

A New Autoxidisable System of the Cell. O. MEYERHOF (*Pflüger's Archiv*, 1923, **199**, 531—566).—Experiments similar to those of Hopkins and Dixon (cf. A., 1923, i, 167) were performed to investigate the oxygen uptake of systems consisting of a sulph-hydryl compound and muscle treated in various ways. The sulph-hydryl compounds employed were thioglycollic acid and cysteine. It was found that with a system of thioglycollic acid and the dried muscle powder prepared according to Hopkins and Dixon, the uptake of oxygen might be twelve times the amount necessary to convert the sulph-hydryl compound to the corresponding disulphide. It was then found that after prolonged extraction with alcohol and ether the muscle powder lost its power of taking up oxygen, this power being retained in a substance precipitated by acetone from the concentrated ethereal extracts. Next it was shown that a mixture of lecithin and thioglycollic acid reacted in the same way as the muscle powder, and finally, that, of the constituents of lecithin, linolenic acid alone possessed this property. It is therefore probable that linolenic acid is the heat stable substance of unspecified nature described by Hopkins and Dixon.

All the above reactions proceed best in an acid solution (p_H about 3), and may be entirely inhibited in neutral or alkaline solution; moreover, the uptake of oxygen ceases when the reaction for the –SH group disappears. The amount of oxygen taken up is about 5 c.c. per g. of dried muscle, or, in the case of linolenic acid, two molecules of oxygen to each molecule of acid; estimation of the iodine value before and after oxidation shows that only two of the double bonds have disappeared; these must therefore have been oxidised to a peroxide linking

$$\begin{matrix}\text{CH}\\ \|\\ \text{CH}\end{matrix} + O_2 \rightarrow \begin{matrix}\text{CHO}\\ |\\ \text{CHO}\end{matrix},$$

as is known to occur in the spontaneous oxidation of linolenic acid.

A close analogy is drawn between the oxidation of lecithin in these experiments and that which takes place in the presence of iron.

A consideration of the kinetics of the reaction and of the other experimental facts enumerated leads the author to suggest that the course of physiological oxidation by the agency of such substances as glutathione is not, as generally accepted, 2R·SH+O=

$RS{\cdot}SR+H_2O$, and $RS{\cdot}SR+H_2O+M=2R{\cdot}SH+MO$ (M being an oxidisable constituent of the muscle), but $2R{\cdot}SH+O_2=\begin{matrix}R{\cdot}SH{\cdot}O\\ \|\\ R{\cdot}SH{\cdot}O\end{matrix}$ and $\begin{matrix}R{\cdot}SH{\cdot}O\\ \|\\ R{\cdot}SH{\cdot}O\end{matrix}+2M=2R{\cdot}SH+2MO$.

According to this theory, it is only the reduced form of such a substance as glutathione which actually takes part in this process of tissue oxidation. C. R. H.

The Antagonism between Magnesium- and Calcium-ions. W. Baumecker (*Biochem. Z.*, 1923, **142**, 142—158).—Magnesium and calcium chlorides inhibit the imbibition of water by fibrin to the same extent, whereas on muscle pulp the former, in certain low concentrations, causes an increased, the latter a diminished imbibition, whilst mixtures of the two salts show a balanced antagonistic action. On the living isolated frog-muscle, the narcotic action of magnesium is unaccompanied by imbibition until the narcosis has become irreversible. Calcium salts cause a marked loss of water. Unlike sodium salts, calcium does not remove the reversible paralysis caused by magnesium. The antagonism between magnesium and calcium on the living muscle is therefore not brought about by their action in causing imbibition or loss of water, but is effected through the myoneural junction. The narcotic action of magnesium on the end-plate is only observed in Ringer solutions containing calcium. It is concluded that magnesium replaces the calcium which is necessary for the proper functioning of the end-plates. J. P.

Behaviour of Calcium Phosphate and Calcium Carbonate (Bone Salts) precipitated in various Media, with Applications to Bone Formation. J. C. Watt (*Biol. Bull. Marine Biol. Lab.*, 1923, **44**, 280—308).—Calcium phosphate, when precipitated in water or in colloidal solutions, is constantly granular and amorphous in character, and is apparently uninfluenced by the nature of the solution. On the other hand, calcium carbonate, when precipitated in water, shows a great diversity of crystalline form; in colloidal solutions, it exhibits two main forms, irregular crystalline and spherical, respectively. Mixtures obtained by simultaneous precipitation of both salts in the same solution admit of identification of each salt separately. The character of the spherules and crystals is influenced by the presence of normal or pathological constituents of blood, especially lecithin and acetone, and by the hydrogen-ion concentration of the colloidal solution. Large spherules, after persisting for months, may undergo structural change, finally dissolving; the substance is then deposited in the crystalline form. The mechanism of the formation of bone in animals is discussed.

Chemical Abstracts.

A Method of Micro-incineration Applicable to Histochemical Researches. A. Policard (*Bull. Soc. chim.*, 1923, **33**, [iv], 1551—1558).—The author has devised a method of studying the distribution of mineral salts in histological sections. The section

is placed on a platinum slide, carefully dried, then raised to a dull red heat for twelve to fifteen minutes. A very slow current of air facilitates the burning off of the organic matter, and is stated to be preferable to oxygen for that purpose. Glass is inadmissible for the slide material as it softens at the temperature required for the operation. Unglazed porcelain may be used. The ash resulting from the incineration forms a "mineral plan" of the section dealt with. This is examined microscopically by reflected light, and it is stated that this examination clearly shows the distribution and relative quantities of mineral matter. The presence and distribution of iron, in particular, is readily studied by the intensity of coloration of the ash by the ferric oxide resulting from the combustion. H. J. E.

Asteriasterol—a New Sterol from the Starfish and the Sterols of certain other Marine Echinoderms. I. H. Page (*J. Biol. Chem.*, 1923, **57**, 471—476).—A sterol, m. p. about 70°, to which the name *asteriasterol* is given, has been isolated from *Asterias forbesi*. It forms an *acetate*, m. p. 97°, and a *benzoate*, m. p. 125°. The colour reactions which it gives with various sterol reagents are described. The sterols present in *Echinarachnius parma* and *Arbacia punctulata* are identical, and those in *Cumingia tellinoides*, *Choetopterus pergamentaceous*, and *Arenicola cristata*, probably identical, with cholesterol.

Oxycholesterol gives an immediate deep violet coloration with arsenious chloride which changes to bright blue on gently heating and to bright green on vigorously boiling. E. S.

Glycerophosphatase in Human Organs. E. Forrai (*Biochem. Z.*, 1923, **142**, 282—290).—The possibility has been investigated of the presence of glycerophosphatase in various dried human organs examined soon after death. The observations of Grosser and Husler (A., 1912, ii, 367) were confirmed and, in addition, the enzyme was found in the adrenals, thyroids, testes, and in carcinomas. Amyloid kidneys contained less, and in a case of eclampsia muscle contained more than the normal organs. None of the organs in which the enzyme was found is of mesodermal origin. It is supposed that the enzyme originates in the epithelial layers. J. P.

The Distribution of Calcium and Inorganic Phosphorus in Milk. P. György (*Biochem. Z.*, 1923, **142**, 1—10).—That portion of the calcium and inorganic phosphate of human milk and of cow's milk which is indiffusible (50—60% in the former and 30—40% in the latter) diminishes with increasing hydrogen-ion concentration, and at the isoelectric point of casein all the calcium and phosphate of the milk is dialysable. During the tryptic digestion of milk at constant p_H, the diffusible calcium and phosphate increases, and similar results were obtained on a casein solution to which calcium chloride and a phosphate mixture had been added. It is concluded that the non-diffusible calcium phosphate of milk is combined with the casein in the form of a

complex double compound, and not simply adsorbed by the protein (cf. Van Slyke and Bosworth, *J. Biol. Chem.*, 1914, **14**; 1915, **20**; 1916, **24**). J. P.

Copper as a Constituent in Woman's and Cow's Milk. Its Absorption and Excretion by the Infant. A. F. Hess, G. C. Supplee, and B. Bellis (*J. Biol. Chem.*, 1923, **57**, 725—729).—Raw cow's milk contains 0·55 mg. of copper per litre and commercially pasteurised milk 0·6—0·7 mg. per litre. Analyses of two specimens of human milk gave values of 0·4 and 0·61 mg. per litre, respectively. The constant presence of copper in the urine of both infants and adults indicates that it is absorbed from the alimentary canal. E. S.

Urinary Acidity. II. The Increased Acidity produced by Eating Prunes and Cranberries. N. R. Blatherwick and M. L. Long (*J. Biol. Chem.*, 1923, **57**, 815—818).—The increased acidity of the urine which is produced by eating prunes or cranberries (A., 1914, i, 627) is due to the excretion of hippuric acid. The benzoic acid present in the fruit appears to be insufficient to account for all the hippuric acid excreted, which must therefore be derived from some other source. E. S.

Synthesis of Hippuric Acid in the Animal Organism. VI. The Influence of the Protein of the Diet on the Synthesis and Rate of Elimination of Hippuric Acid after the Administration of Benzoates. W. H. Griffith and H. B. Lewis (*J. Biol. Chem.*, 1923, **57**, 697—707; cf. A., 1923, i, 1261).—The rate of synthesis of hippuric acid by rabbits, following the administration of sodium benzoate, is increased when the hydrolytic products of proteins containing glycine are administered simultaneously with the benzoate, but not when the proteins do not contain this amino-acid. It is therefore improbable that any readily available precursors of glycine are produced during the ordinary metabolism of proteins. E. S.

Allantoin. I. The Influence of Amino-acids on the Excretion of Allantoin by the Rabbit. A. A. Christman and H. B. Lewis (*J. Biol. Chem.*, 1923, **57**, 379—395).—The excretion of allantoin by rabbits was decreased markedly by the administration of amino-acids (glycine, alanine, glutamic acid) or urea, and to a smaller degree by gelatin. E. S.

Several Cases of Cystinuria. J. M. Looney, H. Berglund, and R. C. Graves (*J. Biol. Chem.*, 1923, **57**, 515—531).—Using recent methods of estimation, the authors have examined several cases of cystinuria and have confirmed older work. The total amount of cystine excreted is composed of two fractions: a small and constant amount derived from endogenous metabolism, and a larger fraction which is proportional to the protein intake. An increased excretion of cystine is not accompanied by an increased elimination of other amino-acids. In the absence of the administration of sodium hydrogen carbonate or of atophan, practically

the whole of the neutral sulphur in the urine is due to cystine; the administration of sodium hydrogen carbonate, however, decreases the excretion of cystine and disturbs the distribution of the neutral sulphur. E. S.

The Proteic Acids of the Urine. III. Oxyproteic Acid. S. EDLBACHER (*Z. physiol. Chem.*, 1923, **131**, 177—178; cf. *Z. physiol. Chem.*, 1922, **120**, 71; **127**, 186).—The so-called "oxyproteic acid" of urine appears to consist essentially of urea, contaminated with some impurities, as it is decomposed by urease with the formation of ammonia, and gives the characteristic crystalline compound with Naphthol Yellow-S (dinitronaphtholsulphonic acid). These results agree with those of Freund and Sittenberger-Kraft (A., 1923, i, 511). W. O. K.

Fat Metabolism in Avitaminosis. II. The Total Fat, Neutral Fat, Cholesterol, and Cholesterol Ester in the Blood of Normal, Starving, Avitaminosed, and Phosphorus Poisoned Rats. K. ASADA (*Biochem. Z.*, 1923, **142**, 44—52).—The total and neutral fat, cholesterol, and cholesterol ester have been determined in the blood of normal, starving, and avitaminosed rats, with and without simultaneous phosphorus poisoning. The blood-fat is highest in the avitaminosed rat and least in the starved rat. After phosphorus poisoning, the total blood-fat in the normally fed animal is unchanged, in starvation it is increased to approximately the normal level, and in avitaminosis associated with phosphorus administration it is markedly increased, but later sinks to sub-normal values. The variations in the amounts of cholesterol and of the ester are parallel to the changes in total fat under the three conditions of experiment. After poisoning with phosphorus, the ester especially is increased, this being most marked in the early stages of avitaminosis. J. P.

Fat Metabolism in Avitaminosis. III. The Fat and Cholesterol Content of the Liver after Phosphorus Poisoning in Normal, Starved, and Avitaminosed Rats. K. ASADA (*Biochem. Z.*, 1923, **142**, 165—180).—In avitaminosed rats, the total and neutral fat of the liver diminishes, but after prolonged vitamin-free feeding it again rises, still keeping within sub-normal limits. The liver cholesterol progressively decreases and does not run parallel to the altered fat content. In the starved animals the diminution of liver fat is marked, whilst the cholesterol is increased. After phosphorus poisoning, which greatly lowers the liver-fat and cholesterol of the starved animal, the liver of the avitaminosed animal is but slightly less rich in fat and cholesterol than that of the normally fed but poisoned rat, but both show a much greater fat content than do the similarly treated but non-poisoned animals. In advanced avitaminosis the phosphorus poisoned liver, which is practically free from glycogen, contains more fat than the normal poisoned liver. Starved and avitaminosed rats are much more susceptible to death from phosphorus poisoning than are normally fed animals. The water content of avitaminosed livers first in-

creases, then diminishes, in relation to normal conditions. After phosphorus poisoning, it is increased in the starved rat, lessened in avitaminosis, and unchanged in the normal rat. J. P.

The Content of Copper and Zinc in Normal and Carcinomatous Tissues. H. J. TAVERNE (*Nederl. Tijdschr., Geneeskunde*, 1923, **67**, i, 2810—2812; from *Chem. Zentr.*, iii, 946).—In a mammary carcinoma, normal tissue contained 0·94 mg. of copper and 3·74 mg. zinc per kg., whilst the cancerous material contained 0·54 mg. of copper and 3·65 mg. of zinc per kg. G. W. R.

Effect of Treatment with Insulin on the Hydrogen-ion Concentration and Alkali Reserve of the Blood in Diabetic Acidosis. G. E. CULLEN and L. JONAS (*J. Biol. Chem.*, 1923, **57**, 541—552).—The treatment of diabetic patients with insulin causes the alkali reserve and the p_H of the plasma, both of which are lowered, to return concurrently to the normal. E. S.

[Physiological] Action of Acetylene. III. The Gases of the Blood of Rabbits during the Administration of Acetylene. R. SCHOEN and G. SLIWKA (*Z. physiol. Chem.*, 1923, **131**, 131—145; cf. A., 1923, i, 727).—During inhalation of a constant mixture of acetylene and oxygen, the acetylene content of the arterial and venous blood of rabbits gradually increases and saturation is reached after seventeen minutes, 88% saturation being reached after five minutes. The presence of acetylene in the air breathed does not influence the oxygen content of the arterial blood, but the carbon dioxide content constantly decreases. After ceasing the administration of the acetylene, increased breathing occurs and acetylene is rapidly expired. W. O. K.

[Physiological] Action of Acetylene. IV. Critical Remarks on the Action of Acetylene. H. WIELAND (*Z. physiol. Chem.*, 1923, **131**, 146—150).—The author has suggested (A., 1922, i, 497) that ethylene and nitrous oxide differ from other inhalation anæsthetics such as chloroform and ether, as they have no effect on anoxybiotic processes, and now replies to criticisms of this view by Bart (*Verh. Deutsch. pharmakol. Ges.*, 1922, **2**, 7) and by Meyer and Hopff (A., 1923, i, 632). W. O. K.

The Influence of Guanidine on the Frog. K. ŠAHOVIĆ (*Glas. Acad. Sci. Belgrade*, **105**, 42—44).—Injections of a solution of guanidine in the frog causes the same symptoms of tetany as was observed by Paton and Findlay with rabbits, mice, and rats. S. S. M.

Behaviour of Quinoline in the Animal Organism. B. SCHEUNEMANN (*Arch. expt. Path. Pharm.*, 1923, **100**, 51—60).—The three quinoline derivatives, observed by Führer (A., 1906, ii, 692) to occur in the urine after administration of quinoline, have been studied in the urine of the rabbit after oral administration of 20 g. of quinoline tartrate. Two of them have been identified as 8-hydroxyquinoline and 6-hydroxyquinoline; the third one is probably 6-hydroxy-4-quinolone. C. R. H.

Chemistry of Vegetable Physiology and Agriculture.

The rôle of Bacteria in the "Lactic Acid Fermentation of Dextrose by Peptone." III and IV. O. Acklin (*Biochem. Z.*, 1923, **142**, 117—141, 351—359).—III. A further study has been made of the action of bacteria-bearing peptones in producing the fermentation observed by Schlatter (A., 1922, i, 1096) in dextrose–peptone–bicarbonate mixtures. The supposed autocatalytic fermentation (*J.S.C.I.*, 1923, 993A, 1145A) can be fully reproduced in sterile peptones inoculated with bacteria from preparations showing the fermentation. The incubation period and the quantitative course of the process is dependent solely on the extent of active bacterial infection. Schlatter ascribed variations in the activities of different peptones to their variable phosphate content, and postulated the existence of an active organic combination between the peptone and phosphoric acid. The author finds that in peptones poor in phosphates (Witte) added phosphate increases the extent of bacterial fermentation up to a limit determined by the hydrogen-ion concentration. On the other hand, peptones rich in phosphorus (Siegfried) showed no increased fermentation on the addition of phosphates. A careful study has been made of the effect of phosphate and acetate buffers on the p_H of the fermentation mixtures and on the general course of the action of the bacteria. The optimum p_H lies between 6·8 and 7·2, being rather nearer the former value than the latter. If sodium acetate is substituted for sodium hydrogen carbonate the fermentation is still observed but in less degree, as measured by acid or gas formation, which diminish with increasing acetate concentration. During the fermentation in the presence of sodium acetate the p_H becomes more acid than is the case when bicarbonate is present.

IV. The course of the fermentation in inoculated peptone is not appreciably influenced by the sterilisation methods employed. The peptone may be sterilised by ultra-filtration through a De Haën filter of 0·78μ. J. P.

Lactic Acid Fermentation of Dextrose by Peptone. E. Baur (*Z. physiol. Chem.*, 1923, **131**, 65).—The author agrees with Barthel and von Euler (A., 1923, i, 985) that the formation of lactic acid from dextrose in presence of peptone, described by Schlatter (A., 1922, i, 1096) is due to bacterial contamination. W. O. K.

Inhibition of Bacterial Growth by Amino-acids. G. A. Wyon and J. W. McLeod (*J. Hyg.*, 1923, **21**, 376—384).—Amino-acids in appropriate concentrations aid bacterial growth, but in relatively low concentrations they may be inhibitory. Inhibition occurred with ten out of eleven acids studied and with several mixtures rich in amino-acids. The inhibitory concentration varies from 11 to 130 millimols. per litre. The cyclic compounds were inhibitory in the lowest concentrations. Histidine, tyrosine,

tryptophan, and phenylalanine were tested. Of the chain compounds tested, cystine was most inhibitory. *Staphylococcus aureus* was able to split glycine in a high but sub-inhibitory concentration. A polypeptide medium may prove valuable for bacterial growth.

CHEMICAL ABSTRACTS.

Catalase in Bacteria and its relation to Anaërobiosis. A. B. CALLOW (*J. Path. Bact.*, 1923, **26**, 320—325).—Comparative estimations were made of the catalase content of nine anaërobes and twelve aërobes. None of the former, and only streptococci among the latter, produced gas when treated with hydrogen peroxide. Hydrogen peroxide was not detected when anaërobes were grown anaërobically and then subjected to the action of the air. It could not be shown conclusively that anaërobes can grow aërobically in the presence of catalase. CHEMICAL ABSTRACTS.

Catalase Production and Sensitiveness to Hydrogen Peroxide among Bacteria: a Scheme of Classification based on these Properties. J. W. MCLEOD and J. GORDON (*J. Path. Bact.*, 1923, **26**, 326—331).—When the characteristics of sensitiveness to hydrogen peroxide, power of producing catalase, and power of producing hydrogen peroxide are taken into account, bacteria can be roughly divided into four groups: (1) those extremely sensitive to hydrogen peroxide and devoid of catalase (the anaërobes), potential peroxide producers; (2) those moderately sensitive to hydrogen peroxide and devoid of catalase (the peroxide producers); (3) those moderately sensitive to hydrogen peroxide and devoid of catalase, but not peroxide producers; and (4) those sensitive to hydrogen peroxide in varying degrees and producers of catalase (the majority of facultative anaërobes).

CHEMICAL ABSTRACTS.

Reduction of Sulphites by certain Bacteria in Media containing a Fermentable Carbohydrate and Metallic Salts. W. J. WILSON (*J. Hyg.*, 1923, **21**, 392—398).—In media containing sodium sulphite, dextrose, and iron salts, reduction of sulphite to sulphide is effected by *Bacillus typhosus*, *B. enteritidis*, *B. paratyphosus B*, and other members of the Salmonella group, but not by *B. paratyphosus A* and the dysenteriæ bacilli.

CHEMICAL ABSTRACTS.

Toluenated Yeast is not Dead. IGOR ASHESHOV and I. GJAJA (*Glas. Acad. Sci. Belgrade*, **105**, 50—57).—In a previous paper (*Compt. rend. Soc. Biol.*, 1922, **86**, 703), it was shown that toluenated yeast consumes considerable quantities of oxygen. In order to determine whether this consumption is due to an oxidation of the dead substance or to the vital functions of the yeast, yeast was toluenated by addition of 2% of toluene. When the toluene was removed by animal charcoal, the yeast regained its activity after incubation for a certain time if transferred to a new substrate. The length of incubation required varied according to the duration of the action of the toluene. If the toluene was absorbed immediately after the toluenisation, eighteen hours' incubation caused the

yeast to regain its activity. After seventy-two hours' contact with toluene, incubation for sixty hours was required. S. S. M.

Phytochemical Reduction in the *cyclo*Hexane Series. S. AKAMATSU (*Biochem. Z.*, 1923, **142**, 188—190).—Yeast, actively growing in sugar solutions, reduces inactive 1-methyl*cyclo*hexan-2-one to dextrorotatory 1-methyl*cyclo*hexan-2-ol. J. P.

Growth of Yeast on a Medium of Wholly Synthetic Origin. E. I. FULMER, V. E. NELSON, and A. WHITE (*J. Biol. Chem.*, 1923, **57**, 397—399).—Yeast has been subcultured on a wholly synthetic medium. The carbohydrate employed was Loew's methose, which was synthesised from formaldehyde. E. S.

Relationships between Hydrogen-ion, Hydroxyl-ion, and Salt Concentrations, and the Growth of Seven Moulds. H. W. JOHNSON (*Iowa State Coll. Research Bull.*, 1923, No. **76**, 307—344).—The known extremes of soil reaction, p_H 3·62—9·68, have little or no inhibiting effect on soil moulds. Seven moulds studied show that the degree of acidity necessary to inhibit growth varies from p_H 1·6 to 3·4, and the degree of alkalinity from p_H 9·0 to 11·2. Salts in order of increasing toxicity are: (1) molecule for molecule. Magnesium sulphate, potassium chloride, magnesium chloride, sodium chloride, calcium chloride, sodium sulphate, sodium carbonate, potassium carbonate; (2) g. per litre. Magnesium sulphate, sodium sulphate, potassium chloride, magnesium chloride, calcium chloride, sodium chloride, potassium carbonate, sodium carbonate. All moulds change the reaction of media in which they grow.

CHEMICAL ABSTRACTS.

Citric Acid Fermentation. W. BUTKEWITSCH (*Biochem. Z.*, 1923, **142**, 195—211).—Cultures of *Aspergillus niger* and *Citromyces glaber*, growing in the presence of quinic acid, do not produce citric acid. If calcium carbonate is present, considerable formation of oxalic acid occurs. Sucrose, the hexoses, and glycerol form the best substrates for citric acid fermentation by these fungi, whilst arabinose and mannitol undergo the fermentation to a less extent. Saccharic and gluconic acids do not give rise to citric acid, and are therefore not to be regarded as intermediate stages in the fermentation. Evidence is adduced in favour of the view that the formation of citric acid from the hexoses takes place with intermediate formation of an acid allied to parasaccharinic acid, rather than Euler's view that acetaldehyde is an intermediate. The intermediate acid product is precipitated from the fermentation mixtures by the addition of lead acetate and ammonia. J. P.

The Fermentation of Dextrose by *Fusarium lini*. A. K. ANDERSON and J. J. WILLAMAN (*Proc. Soc. Exp. Biol. Med.*, 1922, **20**, 108—110).—*Fusarium lini*, when grown on dextrose media, produces ethyl alcohol and carbon dioxide as the main by-products of metabolism. Succinic acid was not produced in appreciable amount. In the absence of dextrose, this organism can utilise ethyl alcohol, preferably at a concentration of 2%.

CHEMICAL ABSTRACTS.

Chemical Composition of the Walls of certain Algæ. M. E. WURDACK (*Chio J. Sci.*, 1923, **23**, 181—191).—The cell-walls of representatives of *Vaucheria*, *Cladophora*, *Oedogonium*, *Spirogyra*, *Zygnema*, and *Draparnaldia* are composed of an inner layer of cellulose and an outer layer of pectose or chitin; when the last-named is present, pectose forms a middle layer. In some forms (*Vaucheria*, *Draparnaldia*), the pectose is difficultly permeable to an ammoniacal solution of cupric oxide and a solution of iodine in potassium iodide; in others (*Cladophora glomeratra*, *Oedogonium irregulare*), a third layer of chitin is present, and in *Oedogonium crassum amplum* there is a layer of an unidentified substance. Mucilaginous sheaths of the algæ studied are of pectic compounds, of which pectic acid predominates, with pectose in some cases.

CHEMICAL ABSTRACTS.

Is Gaseous Nitrogen a Product of Seedling Metabolism? J. DAVIDSON (*Bot. Gaz.*, 1923, **76**, 95—101).—Wheat seedlings and cow pea seedlings were grown in Kjeldahl flasks under sterile and non-sterile conditions. The results indicate that no nitrogen in the gaseous form is lost in the process of germination and in the early life of the seedlings as an inherent function of the metabolic processes.

CHEMICAL ABSTRACTS.

The Absorption of Ions by Plants. D. R. HOAGLAND (*Soil Sci.*, 1923, **16**, 225—246).—The results of a comprehensive series of studies on the absorption of ions by barley plants from different solutions are reported. Different ions were absorbed at different rates and the absorption of any one ion was found to be affected by other ions. Thus kations are affected both by kations and anions, and vice versa. For example, potassium is absorbed most rapidly from potassium nitrate, less rapidly from potassium chloride, and least rapidly from potassium sulphate solutions. The proportion of ions absorbed from a solution decreases as their concentration in the solution falls. Ions may be absorbed either more rapidly or less rapidly than water. Thus whilst potassium-, nitrate-, and phosphate-ions may be taken up more rapidly than water, calcium-, magnesium-, and sulphate-ions may be taken up at the same time at a slower rate than water. Attention is directed to the fact that energy exchanges are involved in the process of absorption and that permeability relations alone are inadequate to explain the phenomena of absorption by plants.

G. W. R.

Phase Reversal in Emulsions and Protoplasm. W. SEIFRIZ (*Amer. J. Physiol.*, 1923, **66**, 124—139; cf. *Science*, 1923, **57**, 694).—The effects of various electrolytes (sodium hydroxide, sodium chloride, barium hydroxide, barium chloride, and calcium chloride) in causing phase reversal in emulsions of (1) oil in water and (2) water in oil, prepared with various emulsifying agents, were studied. Olive oil emulsions with casein, gliadin, cholesterol, or cephalin in the aqueous phase, form water in oil systems which are reversible with sodium hydroxide. Oil emulsions, in which saponin (senegin, smilacin), gelatose, gum arabic, albumin, lecithin, or plant extract

is the emulsifier, form oil in water systems which are not reversible with barium chloride. The hypothesis of Clowes (A., 1916, i, 583) on the mechanism of permeability changes in the plasma membrane of organisms is based on the behaviour of only one type of emulsion in the presence of certain ions and must be regarded as a purely speculative hypothesis which rests on very uncertain evidence.

CHEMICAL ABSTRACTS.

Amylase in Plants. III. K. SJÖBERG (*Biochem. Z.*, 1923, **142**, 274—279).—Following the earlier work of the author on the activity of plant amylases (A., 1923, i, 275), it is shown that an amylase is present in tulip plants, which do not form starch in the dark and very little when exposed to light. It occurs in leaves, sepals, stem, and juice, and is more prominent in the young than in the old plants. Amylase is also present in the roots and more especially in the stem and buds of young specimens of *Pisum sativum*. From the fact that the enzyme is most prominent in actively growing plant-tissues, it is assumed to have a synthetic function possibly in forming cellobiose. J. P.

Analysis of the Jerusalem Artichoke. A. T. SHOHL (*J. Amer. Chem. Soc.*, 1923, **45**, 2754—2756).—The juice of the Jerusalem artichoke has p_H 5·0. It contains only traces of water-soluble-*B* vitamin. Analysis of the pared tuber (69 % of total weight) gives moisture, 79·0%; total nitrogen, 3·1% (of which 71·5% is water-soluble, and 27·5% present as amino-acids); fat, 0·2%; carbohydrate (inulin), 15·5%; fibre, 0·8%; ash, 1·1%, in close agreement with the results of Strauss (*Berlin. Klin. Woch.*, 1912, **49**, 1213) and of Langworthy (*U.S. Dept. Agric. Bull.*, 1917, **468**). The metabolism of inulin is discussed and a reinvestigation recommended of the use of the Jerusalem artichoke in the treatment of diabetes.

W. S. N.

Saponins [of Chestnut Seeds]. A. W. VAN DER HAAR (*Rec. trav. chim.*, 1923, **42**, 1080—1083).—It is shown that the saponin from chestnut seeds, if obtained free from accompanying sucrose, does not give rise, on hydrolysis, to lævulose, as stated by Blau (*Diss. Univ. Zürich*, 1911) and Bosshard (*Diss. Tech. Hochschule Zürich*, 1916). The saponin in question contains 9·8% of water, 1% of ash, and, on hydrolysis, affords: sapogenins, 46·2%; dextrose, 23%; pentose, 4·8%; methylpentose, 4·2%; *d*-galactose, 2·24%; *d*-glycuronic acid, 10% (identified as *d*-glycuronolactone); and acetic acid, 3·4%. Xylose, *d*-mannose, fucose, and galacturonic acid are not products of the hydrolysis. E. E. T.

Influence of Hexamethylenetetramine and Formaldehyde on the Haricot Bean. E. NICOLAS and G. NICOLAS (*Compt. rend.*, 1923, **177**, 1062—1064).—A continuation and confirmation of previous work (A., 1923, i, 427), using different varieties of haricot beans. E. E. T.